*Journal of Thermal Analysis, Vol. 13 (1978) 473–487*

# POLYMORPH TRANSITION KINETICS BY DTA

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(Received July 22, 1977)

The polymorph transition kinetics of the changes vaterite to calcite and aragonite to calcite have been followed using a DTA technique. The method eliminates the grinding process present in other analytical techniques and so has certain advantages. For both transitions the kinetic equation describing the process is found to be:

$$\frac{\partial \alpha}{\partial t} = \frac{4}{3} k \left[-\ln (1-\alpha)\right]^{3/4}(1-\alpha).$$

Values of activation energy were found to be 452 ± 19 KJ mole$^{-1}$ and 208 ± 8 KJ mole$^{-1}$ for aragonite and vaterite transitions respectively using a procedure which enabled the calculation of kinetic parameters from a rising temperature experiment.

Quantitative analysis of the calcium carbonate polymorphs calcite, aragonite and vaterite has previously been carried out by X-ray diffraction and infra-red spectroscopy. These methods are suspect owing to possible conversion of metastable vaterite and aragonite into calcite (or calcite into aragonite), during the grinding of specimens below the required 63 $\mu$m for X-ray analysis [1], or below the minimum IR wavelength used, i. e. between 2.5 and 15 $\mu$m [2, 3]. If DTA is used the particle size of the samples need not be less than 63 $\mu$m, and the endothermic transitions of metastable aragonite and vaterite into the stable calcite can be used to determine the polymorph content.

Since there is no weight change during these transitions, conventional methods of determining the kinetics by TG cannot be employed. A dynamic temperature technique is proposed here which may be adapted to determine the kinetics of any polymorph transition by DTA.

## Experimental

Pure synthetic samples of the polymorphs were prepared according to the method of Mazzella [4]. It was found that previous reports on preparing vaterite did not take into account the mode of adding equimolar calcium nitrate to sodium carbonate in the presence of sulphate ions. Mazzella showed that for pure vaterite to be precipitated a very slow initial rate of addition (20 drops per minute) of 0.2 $M$ calcium nitrate to 0.2 *M* sodium carbonate, containing 0.025 *M* sodium sulphate is required. This rate of addition may be increased as the precipitation progresses and also if larger volumes of solutions are employed.

Aragonite was prepared by adding 0.2 *M* calcium nitrate to 0.067 *M* sodium carbonate maintained at 95°. After precipitation both the aragonite and vaterite were vacuum filtered, washed with deionised water and air dried to prevent any transition to calcite.

Pure synthetic calcite was obtained in the form of A. R. calcium carbonate, supplied by B. D. H. Chemicals Ltd.

All these samples were passed through 45 μm B. S. sieves and analyzed for polymorph purity by X-ray diffraction according to the method of Silk and Lewin [5]. Subsequent preparations of the carbonates were periodically checked by this method to ensure no aragonite or vaterite conversion had occurred, as has been observed under certain conditions by several authors [4, 6–8].

### *DTA system*

Samples of aragonite and vaterite were run on the Netzsch DTA to ascertain the most favourable conditions for obtaining well-defined peaks. Owing to the low heat of transition for aragonite → calcite (likewise for vaterite), it was found neces-

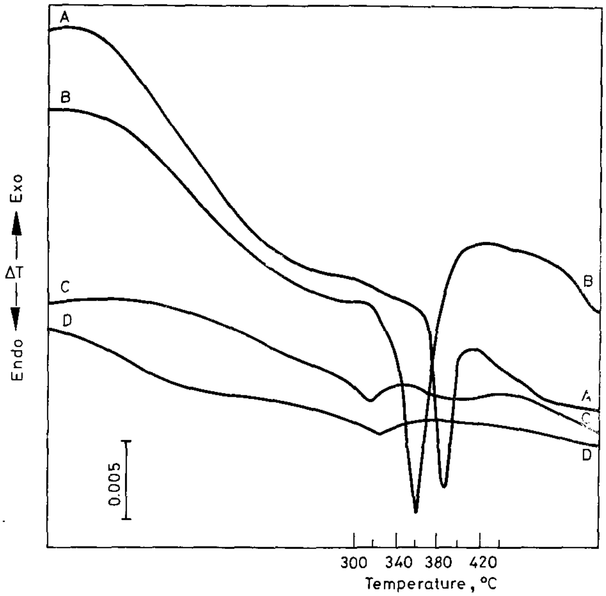

Fig. 1. Effect of sample holder on polymorph DTA curves. A) Aragonite/Nickel integral sample holder; B) Vaterite/Nickel integral sample holder; C) Vaterite/Nickel DDK sample holder; D) Vaterite/Ceramic DDK sample holder

sary to use a system utilizing maximum recording sensitivity whilst minimizing base-line drift and giving a resolution between aragonite and vaterite peaks.

Consequently the following conditions were used for the polymorph analysis: – Heating rate: 10° min$^{-1}$, temperature range: 20 – 300°, sensitivity: 50%, measuring range: ±0.05 mV, thermocouples: Chromel-alumel, sample holder: nickel integral holder 0.4 g sample aliquots, atmosphere: static air, reference material: A. R. calcium carbonate (as calcite) 53 – 63 μm.

For quantitative DTA the DDK sample holder is usually advocated. However, it was found that using both ceramic and nickel DDK sample holders the reduction in peak area and resolution far outweighed the loss of accuracy of using a nickel integral sample holder. A comparison of these DTA curves are shown in Fig. 1.

### *Reproducibility*

Five samples of aragonite and vaterite were analyzed according to the conditions listed in the previous section; the results are given in Table 1. The peak areas of the endotherms were determined by cutting them out and subsequent weighing; figures given for peak areas are equivalent to the weight in mg.

Table 1

Reproducibility of aragonite and vaterite DTA curves

| | Aragonite endotherm peak, °C | Area* |
|---|---|---|
| 1 | 388 | 16.6 |
| 2 | 386 | 16.1 |
| 3 | 387 | 16.5 |
| 4 | 384 | 16.5 |
| 5 | 387 | 15.8 |
| | Vaterite endotherm peak, °C | Area |
| 1 | 358 | 23,5 |
| 2 | 258 | 20.9 |
| 3 | 357 | 21,3 |
| 4 | 358 | 23.2 |
| 5 | 359 | 23,1 |

* All areas quoted in this and subsequent tables are in arbitrary units (see text).

The maximum variation of peak area for both polymorphs is around ±4%, though one sample of vaterite did give a totally erroneous result possibly through impurities being present. Overall there is no basis for using peak height as a means of quantitative determining of polymorph composition – both polymorph transitions gave varying heights of endotherms. The peak temperatures are reasonably accurate, ±3° in both cases, giving transition temperatures of 386° ± 3° and 357° ± 3° for aragonite and vaterite respectively. It should be added that using a dynamic temperature technique, peak temperatures will vary with heating rate and other procedural variables, hence, the figures quoted refer to a heating rate of 10° $\mathrm{min}^{-1}$

### *Polymorph composition in calcite*

0.4 g aliquots aragonite and vaterite were prepared as 20, 40, 60 and 80% polymorph in calcite by mixing with A. R. calcium carbonate having a particle size fraction of 53–63 μm. The results are given in Table 2.

Table 2

Effect of calcite content on aragonite and vaterite DTA curves

| Composition | Aragonite endothermic peak, °C | Area |
|---|---|---|
| 20% Aragonite | 393 | 3.0 |
| 40% Aragonite | 385 | 6.6 |
| 60% Aragonite | 386 | 9.5 |
| 80% Aragonite | 386 | 12.3 |
| 100% Aragonite | 387 | 16.5 |

| Composition | Vaterite endothermic peak, °C | Area |
|---|---|---|
| 20% Vaterite | 364 | 5.2 |
| 40% Vaterite | 365 | 10.1 |
| 60% Vaterite | 363 | 16.2 |
| 80% Vaterite | 360 | 20.0 |
| 100% Vaterite | 359 | 20.9 |

The main consideration is whether or not quantitative results can be obtained using an integral specimen holder rather than DDK holders. From the plot of peak area *v.* % polymorph in Fig. 2 it is seen that for aragonite a near linear relationship is obtained whereas a trailing off is found between peak area and composition of vaterite. Mackenzie suggests that good quantitative DTA work should be within ±2% error [9]. It was found that the above method involved errors of less than ±4%, which one may assume to be within the boundaries of quantitative analysis.

Also noted from Table 2 is the slight increase in peak temperature with increase in calcite concentration, an indication of the dilution effect.

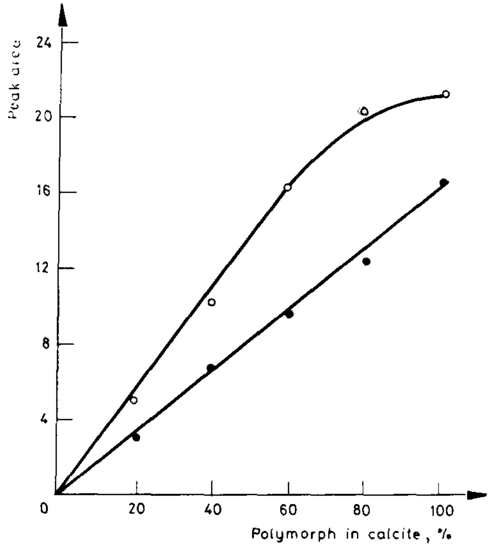

Fig. 2. Effect of calcite content on polymorph DTA peak area. ○ Vaterite; ● Aragonite

## *Effect of sample weight*

The design of the integral sample holder indicates that varying quantities of sample can be contained, providing of course the thermocouples are covered. 0.30,

Table 3

Effect of sample weight on aragonite and vaterite DTA curves

| Sample weight, g | Aragonite endothermic peak, °C | Area |
|---|---|---|
| 0.325 | Insufficient sample covering thermocouples, resulting in severe curve oscillation | |
| 0.35 | 406 | 18.6 |
| 0.375 | 402 | 25.6 |
| 0,40 | 387 | 16.5 |
| **Sample weight, g** | **Vaterite endothermic peak, °C** | **Area** |
| 0.30 | Insufficient sample | |
| 0,325 | 359 | 25.1 |
| 0.35 | 360 | 23.5 |
| 0.375 | 359 | 26.8 |
| 0.40 | 358 | 23.2 |

0.325, 0.35, 0.375 and 0.4 g of both polymorphs were analyzed under the usual conditions.

From Table 3 the results do not indicate any correlation between sample weight and peak area, nor is there any relationship between sample weight and peak temperature. Obviously the quantity of material above the thermocouple affects the thermal diffusivity of the system, hence, the peak characteristics [10]. Therefore, using an integral sample holder quantitative data may be obtained providing that the calibration and subsequent analyses are of the same sample weight and packing.

### *Effect of particle size*

Over 90% of the synthetic polymorphs passed through the finest B. S. sieve of 45 μm. Consequently to test the effect of varying particle size fractions on the DTA curves the reference material rather than the samples was separated into sieve fractions. A. R. calcium carbonate was sieved into the following particle size ranges: 106 – 75μm, 75 – 63μm, 63 – 53 μm, 53 – 45 μm and ≤45 μm. Analyses were carried out on the vaterite polymorph, results of which are given in Table 4.

Table 4

Effect of reference particle size on vaterite DTA curves

| Size fraction, μm | Peak, °C | Area |
|---|---|---|
| 45 | 360 | 18.2 |
| 45–53 | 362 | 18.2 |
| 53–63 | 359 | 18.3 |
| 63–75 | 353 | 18.6 |
| 75–106 | 353 | 18.8 |

Little difference is observed with increase in particle size of the reference material, except for what appears to be an erroneous result for the 63 – 53 μm fraction. The reduction in peak temperature as the reference particle size increases is probably the converse noted previously [9], in which the peak temperature increases as the particle size increases. Also correlated with Mackenzie's observations is the negligible difference (around ±1.5%) of the peak area with respect to the particle size. This may indicate the transition involves a surface or nucleation process.

### *Transition kinetics*

Determination of reaction kinetics by DTA has been studied by many authors notably Kissinger [11], and Borchardt and Daniels [12]. A review by Sharp [13] gives theoretical objections to the method of Kissinger, only Borchardt and Daniels method is considered valid. Three initial assumptions to this work are made:

1. The temperatures within the sample holders are uniform i. e. $T = T_s - T_r$, where $T_s$ and $T_r$ are the single temperatures of the sample and reference, respectively. This can only be achieved by stirred dilute solutions.
2. Heat transfer through the sample and reference is only by conduction, hence, the heat transfer coefficient, $K$, is identical for both.
3. Heat capacities of sample and reference are equal, this is applicable within reason providing the solutions are dilute.

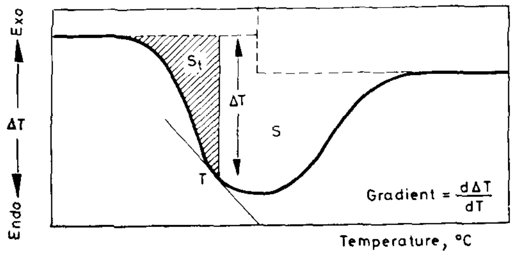

Fig. 3. A typical DTA endotherm. $S_t$ = Area under peak at temperature I.; $S$ = Total peak area

By definition the polymorphs aragonite, calcite and vaterite are all calcium carbonate, therefore, one can safely assume their heat transfer coefficients and heat capacities are similar. Thus, conditions (2) and (3) above are satisfied. Borchardt and Daniels [12] state that condition (1) cannot be satisfied exactly by solids. However, an approximation may be made by taking the single temperatures from a fixed point within the sample and reference, a suitable point being the thermocouples.

A typical DTA endotherm is shown in Fig. 3 and relationship between temperature (or time) and change in enthalpy is noted. For the endothermic transition of aragonite (or vaterite) → calcite, the decrease in enthalpy of the sample equals the heat absorbed during the transition plus the heat transferred to the holder from the surroundings.

For the sample holder:

$$-C\partial T_s = -\partial H + K(T_b - T_s)\partial T. \qquad (1)$$

For the reference holder:

$$C\partial T_r = K(T_b - T_r)\partial T \qquad (2)$$

where $C$ is the heat capacity of the calcium carbonate,

$\partial T_s$, $\partial T_r$ are the changes in sample and reference temperatures,

$\partial H$ is the heat evolved during an increase in temperature $\partial T$.

The heat of transition is the difference between Eqs (2) and (1).

$$C(\partial T_r - \partial T_s) = \partial H + K(T_s - T_r)\partial T. \qquad (3)$$

Also, $\Delta T = T_r - T_s$

$$\therefore \qquad C\partial\Delta T = \partial H - K\Delta T\partial T \tag{4}$$

The total heat of reaction occurs between $T = 0$ and $T = \infty$, thus:

$$\Delta H = C(\Delta T_\infty - \Delta T_0) + K\int_0^\infty \Delta T\partial T \tag{5}$$

At $T = 0$, $\Delta T = 0$; At $T = \infty$, $\Delta T = 0$

$$\Delta H = K\int_0^\infty \Delta T\partial T$$

$$\Delta H = KS \tag{6}$$

where $S$ is the total peak area. $\Delta H$ is the heat absorbed by the transition of $m_0$ moles of polymorph originally present. In a temperature interval $\partial T$ the heat evolved $\partial H$ is directly proportional to the number of moles transforming, $\partial m$.

$$-\partial H \infty \partial m$$

$$\frac{-\partial H}{\Delta H} = \frac{\partial m}{m_0}$$

$$\partial H = -\left(\frac{KS}{m_0}\right)\partial m. \tag{7}$$

Substituting $\partial H$ in Eq. (4):

$$C\partial\Delta T = -\left(\frac{KS}{m_0}\right)\partial m - K\Delta T\partial T$$

$$= \frac{\partial m}{\partial T} = \left(\frac{m_0}{KS}\right)\cdot\left(\frac{C\partial\Delta T}{\partial T} + K\Delta T\right). \tag{8}$$

That is, the rate of reaction $\partial m/\partial T$ is related to the slope of the DTA curve $\partial\Delta T/\partial T$ and peak height $\Delta T$.

The number of moles, $m$, of polymorph present at temperature $T$ is the original number of moles, $m_0$, minus the number of moles which have undergone transition.

$$\text{i. e. } m = m_0 - \int_0^T - \left(\frac{\partial\alpha}{\partial T}\right)\partial T \tag{9}$$

Substituting the rate of reaction:

$$m = m_0 - \left(\frac{m_0}{KS}\right)\left[C\int_0^T\left(\frac{\partial\Delta T}{\partial T}\right)\partial T + K\int_0^T \Delta T\partial T\right]$$

$$m = m_0 - \left(\frac{m_0}{KS}\right)\cdot(C\Delta T + KS_T). \tag{10}$$

Where $S_T$ is the fraction of the peak area at temperature $T$.

$$\frac{m_0 - m}{m_0} = \left(\frac{1}{KS}\right) \cdot (C\Delta T + KS_T).$$

Also, $\alpha = \frac{m_0 - m}{m_0}$ i. e. the fraction of polymorph transformed.

$$\text{Then } \alpha = \left(\frac{1}{KS}\right) \cdot (C\Delta T + KS_T) \tag{11}$$

$$\alpha = \frac{C\Delta T}{KS} + \frac{S_T}{S}.$$

Since $C\Delta T$ is small and $KS$ is large, then to a first approximation:

$$\alpha = \frac{S_T}{S} \tag{12}$$

i. e. The fraction transformed at temperature $T$ is the ratio of the peak area at temperature $T$ compared to the total peak area.

The rate of transition with respect to time is given by:

$$\frac{\partial\alpha}{\partial t} = Kf(\alpha) \tag{13}$$

where $k$ is the rate constant,

also, $\frac{\partial\alpha}{\partial T} = \frac{\partial\alpha}{\partial t} \cdot \frac{\partial t}{\partial T}$.

Where $\frac{\partial T}{\partial t} = \beta$, the heating rate.

$$\frac{\partial\alpha}{\partial T} = \frac{k \cdot f(\alpha)}{\beta}$$

$$\left(\frac{\frac{\partial\alpha}{\partial T}}{f(\alpha)}\right) = \frac{A \cdot e^{-E/RT}}{\beta}$$

$$\ln\left(\frac{\frac{\partial\alpha}{\partial T}}{f(\alpha)}\right) = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT}. \tag{14}$$

The above equation was originally developed by Achar [14] for application to thermogravimetry. By plotting *ln* $((\partial\alpha/\partial T)/f(\alpha))$ against $1/T$ the gradient will be $-E/R$ and the intercept *ln* $(A/\beta)$. The values $\partial\alpha/\partial T$ are the tangents to the curve of $\alpha$ against $T$ (Fig. 4), which are derived from Eq. (12). The function $f(\alpha)$ is established from the differential form of the standard rate equations.

Originally Eq. (13) was considered valid only for isothermal conditions, MacCallum and Tanner [15] suggesting that $\alpha$ is a function of time and temperature only.

i. e. $\alpha = f\ (t,T)$

$$\partial\alpha = \left(\frac{\partial\alpha}{\partial t}\right)_T \partial t + \left(\frac{\partial\alpha}{\partial T}\right)_t \partial T$$

$$\frac{\partial\alpha}{\partial t} = \left(\frac{\partial\alpha}{\partial t}\right)_T + \left(\frac{\partial\alpha}{\partial T}\right)_t \cdot \beta$$

$\left(\frac{\partial\alpha}{\partial t}\right)_T$ is the rate of reaction with respect to time at (an isothermal) temperature $T$, this being equal to $\partial\alpha/\partial t$ only at $\beta = 0$. However, it is argued by Felder and Stahl [16] that $(\partial\alpha/\partial T)_T$, the rate of reaction with respect to temperature at time $t$ is zero,

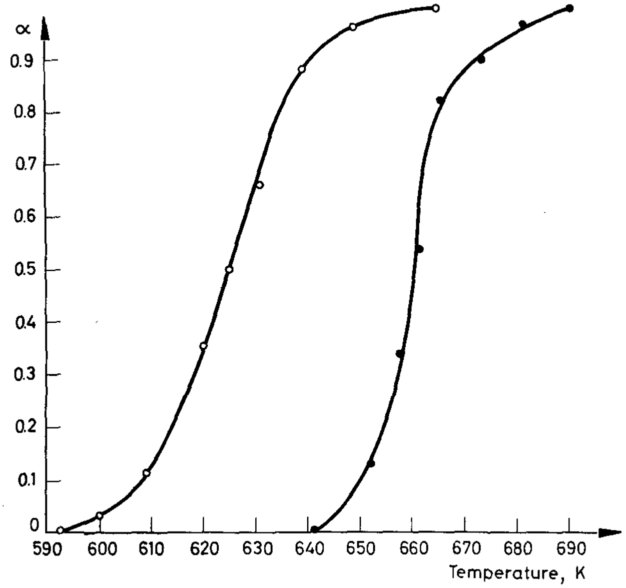

Fig. 4. Plot of $\alpha$ v. I for polymorph transitions. ▲ Vaterite; ● Aragonite

and therefore, the conclusion is that $\alpha$ is a function of time, temperature and also the reaction path taken. Hence the generalized rate Eq. (13) is valid for dynamic temperature systems.

Using the differential method of Achar two disadvantages are evident. Firstly, the inaccuracy of determining $\partial\alpha/\partial T$ as the tangents to the curve $\alpha$ v. $T$, and secondly, the substitution of the correct rate equation(s) for $f(\alpha)$ according to the region of $\alpha$. By developing a computer programme to determine the tangents from the plot of $\alpha$ $v.$ $t$ aritmetical errors will be minimized. An extension to the programme would be the calculation of Eq. (14) using a series of rate equations for $f(\alpha)$, the correct rate equation being the one which gives the best straight-line fit.

The results presented here were determined by a trial-and-error approach of calculating Eq. (14) by substituting a total of fourteen rate expressions, in their corresponding region of $\alpha$, to determine the best straight-line fit to the equation. The rate expressions substituted for $f(\alpha)$ are listed below:

Mampel Power Law $\frac{\partial \alpha}{\partial t} = 2kt$ (i. e. $f(\alpha) = 2t$)

Mampel Power Law $\frac{\partial \alpha}{\partial t} = 3kt^2$

Mampel Power Law $\frac{\partial \alpha}{\partial t} = 4kt^3$

Contracting Sphere Model $\frac{\partial \alpha}{\partial t} = 3/2k(1 - \alpha)^{\frac{1}{3}}$

Contracting Sphere Model $\frac{\partial \alpha}{\partial t} = 2k(1 - \alpha)^{\frac{1}{2}}$

Contracting Sphere Model $\frac{\partial \alpha}{\partial t} = 3k(1 - \alpha)^{\frac{2}{3}}$

1st Order Decay Law $\frac{\partial \alpha}{\partial t} = k(1 - \alpha)$

Avrami-Erofeev eqn. $\frac{\partial \alpha}{\partial t} = 4/3k(-\ln(1 - \alpha))^{\frac{1}{4}}(1 - \alpha)$

Avrami-Erofeev eqn. $\frac{\partial \alpha}{\partial t} = 2k(-\ln(1 - \alpha))^{\frac{1}{2}}(1 - \alpha)$

Avrami-Erofeev eqn. $\frac{\partial \alpha}{\partial t} = 3k(-\ln(1 - \alpha))^{\frac{2}{3}}(1 - \alpha)$

Ginstling and Brounshtein Eq. $\frac{\partial \alpha}{\partial t} = 3/2k((1 - \alpha)^{\frac{1}{3}} - 1)^{-1}$

One-Dimensional Diffusion $\frac{\partial \alpha}{\partial t} = 1/2k\,\alpha^{-1}$

Two-Dimensional Diffusion $\frac{\partial \alpha}{\partial t} = k(-\ln(1 - \alpha))^{-1}$

Jander Eq. $\frac{\partial \alpha}{\partial t} = 3/2k(1-(1 - \alpha)^{\frac{1}{3}})^{-1}(1 - \alpha)^{\frac{2}{3}}$.

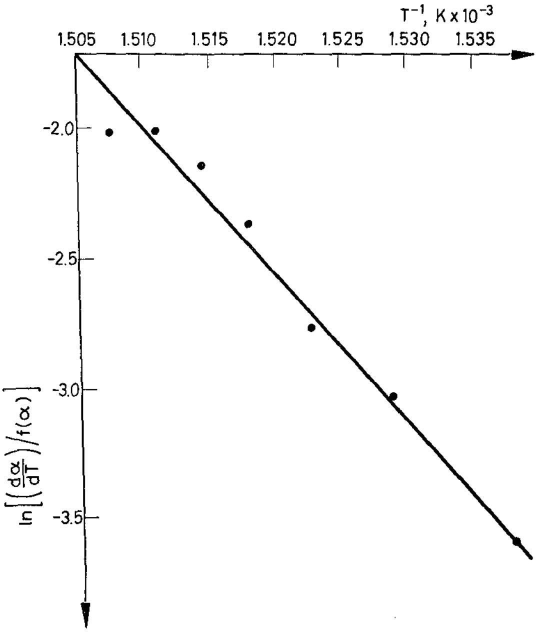

Fig. 5. Aragonite transition kinetics

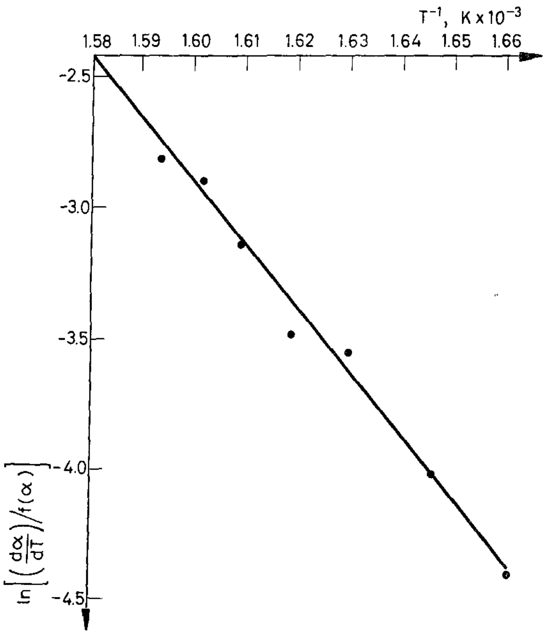

Fig. 6. Vaterite transition kinetics

For both transitions and Avrami-Erofeev equation applies, where $f(\alpha) = 4/3(-\ln(1-\alpha)^{3/4}(1-\alpha))$ between $\alpha$ 0.05 and $\alpha$ 0.7. Values of activation energy were found to be $452 \pm 19$ *KJ.* mole$^{-1}$ and $208 \pm 8$ *KJ.* mole$^{-1}$ for aragonite and vaterite transitions respectively. The gradient from which these results were calculated are shown in Figs 5 and 6.

Although there are no literature values for the activation energy of vaterite transition, aragonite kinetics have been noted previously [17, 18]. Davis and Adams obtained a value of 443 *KJ*·mole$^{-1}$ by an X-ray diffraction/pressure technique, while the isothermal/IR. system of Rao gave an activation energy of 397 *KJ.* mole$^{-1}$.

The pre-exponential values were calculated to be $1.3 \cdot 10^{34}$ and $6.7 \cdot 10^{15}$ for aragonite and vaterite transitions respectively. Although the value for vaterite is in the region expected for unimolecular bulk decomposition according to Cordes [19] and Shannon [20], the pre-exponential value for the aragonite transition is far greater than expected. Variations in $\partial\alpha/\partial T$ may account for this error but in doing so a lower activation energy will result.

## Conclusions

Application of DTA for the quantitative analysis of the calcium carbonate polymorphs is feasible under a spectrum of particle sizes though limitations on the system are the time for analysis, sensitivity and accuracy using integral sample holders. For routine work an instrument with a means of quick cooling, fast heating rates and a finer measuring range would be the most suitable.

With respect to polymorph transition kinetics it has been shown that DTA offers a suitable method of determining the mechanism of a reaction which does not involve a weight change or change in pysical state – parameters that afford the classical isothermal approach of determining reaction kinetics. Providing the reaction under investigation only involves a change in polymorphic state then the method given here should be applicable. Drawbacks to this technique mentioned in the previous section are arithmetical errors and the time-consuming approach of linear regression analysis to determine the correct mechanism. Both these difficulties may be overcome by a suitable computer programme.

Two possible limitations to this technique may be (*a*) the coincidence of data giving two or more perfect straight-line fits of $\ln((\partial\alpha/\partial t)/f(\alpha))$ against $1/T$, and (*b*) continual changes in rate mechanisms as increases. Such occurences will probably lead to varying gradients of the above plots, and therefore varying activation energies. Although this was not observed with calcium carbonate polymorph transitions the possibility should not be ruled out.

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One of the authors (P. D.) wishes to thank Dr. J. H. Sharp, (Dept, of Ceramics, Glass and Polymers, University of Sheffield, U. K.), for his critical discussion of the manuscript, and the Science Research Council for the studentship awards to undertake and present this work.

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Résumé — La cinétique de la transition polymorphe de la vatérite en calcite et celle de l'aragonite en calcite ont été suivies par ATD. Cette méthode élimine l'opération de broyage nécessaire avec les autres techniques analytiques, ce qui présente un avantage certain. Les deux transitions peuvent être décrites par l'équation cinétique suivante:

$$\frac{\partial\alpha}{\partial t} = \frac{4}{3}k[-\ln(1-\alpha)]^{3/4}(1-\alpha)\,.$$

Les valeurs de l'énergie d'activation ont été trouvées égales à 452 ± 19 kJ mol$^{-1}$ et 208 ± 8 kJ mol$^{-1}$ pour les transitions respectives de l'aragonite et de la vatérite, par un procédé permettant le calcul des paramètres cinétiques à partir d'un essai effectué à température croissante.

Zusammenfassung — Die Übergangskinetik der polymorphen Änderungen von Vaterit zu Calcit und Aragonit zu Calcit wurde unter Anwendung der DTA-Technik verfolgt. Bei der Methode erübrigt sich der bei anderen analytischen Verfahren notwendige Mahlprozess, was von gewissem Vorteil ist. Für die Beschreibung der Prozesse beider Übergänge wurde folgende kinetische Gleichung gefunden:

$$\frac{\partial\alpha}{\partial t} = \frac{4}{3}k[-\ln(1-\alpha)]^{3/4}(1-\alpha)\,.$$

Als Aktivierungsenergien wurden Werte von 452 ± 19 KJ Mol$^{-1}$ und 208 ± 8 KJ Mol$^{-1}$ für die Übergänge von Vaterit bzw. Aragonit gefunden. Hierzu wurde eine Methode eingesetzt, die die Berechnung der kinetischen Parameter aus einem Versuch mit steigender Temperatur gestattet.

Резюме — Кинетика полиморфного перехода ватерита до кальцита и арагонита до кальцита была прослежена с помощью метода ДТА. Этот метод устраняет процесс измельчения, используемый в других аналитических методах, вследствии чего обладает определенным преимуществом. Было найдено, что процесс обоих переходов может быть описан кинетическим уравнением:

$$\frac{\partial \alpha}{\partial t} = \frac{4}{3} k[-\ln(1-\alpha)]^{3/4}(1-\alpha).$$

Используя метод, который позволяет вычислять кинетические параметры из поднимающейся температуры эксперимента, были найдены энергии активации переходов для арагонита и ватерита, которые соответственно равны 452 ± 19 и 208 ± 8 кдж/моль.