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Critical examination of the DTA techniques used to study the kinetics of solid-state transformations

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The use of the different equations proposed to study the kinetics of the glass-to-crystal transition from DTA curves has been extended to include the evaluation of the kinetic parameters of polymorphic transitions. The transformation kinetics of $CaCO_3$ (aragonite to calcite) and PbO (litharge to massicot) are the examples studied. The kinetic results of both transformations, obtained by the analysis of DTA curves, differ widely from those revealed by the analysis of the isothermal kinetic data. This discrepancy is probably due to erroneous simplifications used in deriving the equations applied in non-isothermal conditions.

1. Introduction

Recently, Marotta *et al.* [1–5] and Lasocka [6] have emphasized the usefulness of differential thermal analysis (DTA) techniques for studying the kinetics of the crystallization of glass. According to these authors, the dynamic methods developed are rather quicker and less laborious than the experiments required under isothermal conditions, which is the usual procedure for studying the kinetics of solid-state reactions.

However, it is noteworthy that the method proposed by Marotta *et al.* [1–5] are actually based upon two assumptions of Piloyan *et al.* [7]. Firstly, the deviation from the baseline, ΔT (T is temperature), is proportional to the reaction rate. Secondly, the temperature increase has a much larger effect on the change in ΔT than on the change in the $f(\alpha)$ function, which is related to the reaction mechanism. However, care must be taken with the kinetic parameters obtained by these methods, in case Piloyan's assumptions are untrue. In fact, Sopick-Lizer and Pawlowski [8] have found a significant change in the function $f(\alpha)$ with increasing temperature.

In this paper we intend to examine the applicability of the dynamic models proposed by Marotta *et al.* [1–5] to study the kinetics of polymorphic transformations, which are similar in nature to the crystallization processes. Two phase transitions of different structural changes – aragonite/calcite (A → C), first-coordination transformation and litharge/massicot (L → W), higher-coordination transformation – have been chosen as test reactions to check the validity of the simplications of Piloyan *et al.* [7]. These simplifications are repeatedly used by Marotta *et al.* in deriving the non-isothermal kinetic equations. Isothermal methods were also used to obtain reliable kinetic data for comparison with kinetic parameters obtained with the DTA technique. A fuller discussion of the results obtained under isothermal conditions will be published elsewhere [9, 10].

2. Experimental procedures

Pure synthetic aragonite and litharge – free of other polymorphs as revealed by X-ray diffraction – were prepared in accordance with the methods

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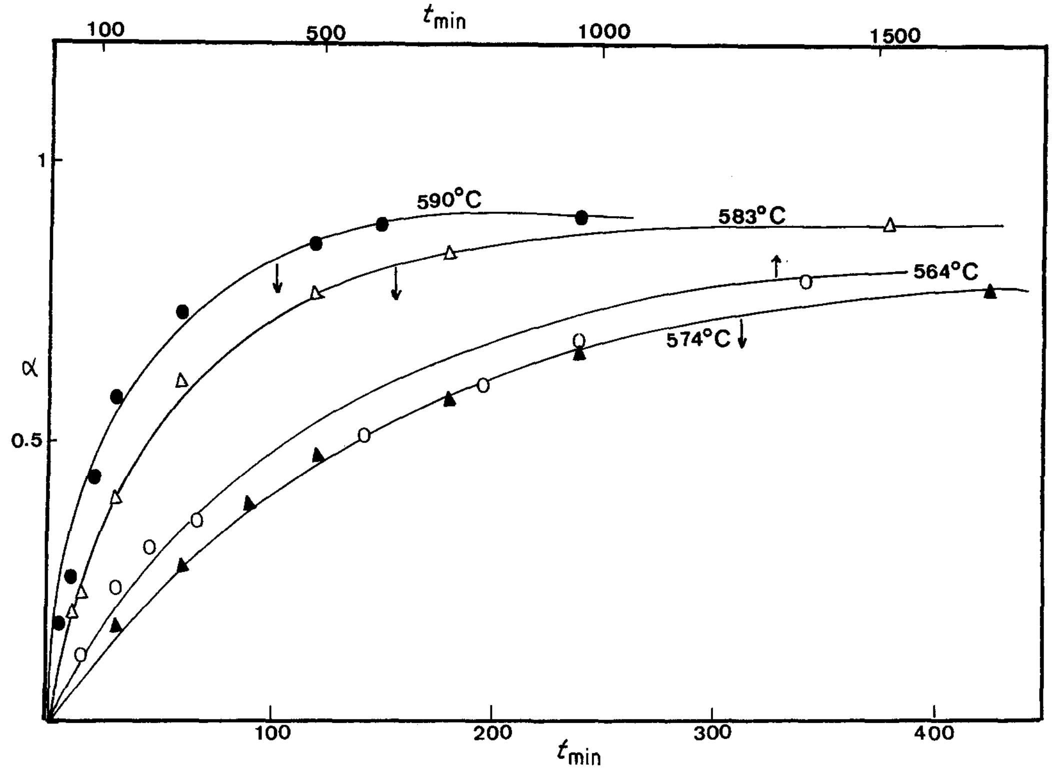

Figure 1 Kinetic transformation of PbO_t (litharge) to PbO_0 (massicot) between 564 and 590° C.

of Rao and Yoganasimhan [11] and Pascal [12], respectively. Grains which passed through a 325 mesh sieve were used as starting material.

The extent of the transformation of aragonite [9] was measured by infrared spectroscopy according to the method developed by Rao and Murthy [13]. Analysis of litharge and massicot was carried out by powder X-ray diffraction methods. The proportions of polymorphs were determined according to the method of Senna and and Kuno [14] by calibrating the intensity ratio $(1\,1\,0)_L/(1\,1\,0)_L + (2\,0\,0)_M$ with standard samples of litharge and massicot.

The DTA diagrams were recorded on a Stanton Redcroft model 673-4 instrument, with heating rates in the range 2 to 20° C min^{-1}. Calcined alumina was used as the reference material. However, in the case of the L → M phase transition, no significant changes were found by using massicot as the reference material.

3. Results and discussion

3.1. Isothermal kinetics

According to previously published kinetic data, the A → C transformation follows a first order rate equation, based upon a random nucleation and fast growth of nuclei [9]. An activation energy of 134 ± 15 kcal mol^{-1} (1 cal = 4.184 J) was calculated from the Arrhenius plot. The high activation energy obtained is probably due to the mechanism of the transformation which may involve the breaking of the first-coordination bonds, since the A → C transformation of $CaCO_3$ is a typical example of reconstructive transformation [15].

The kinetics of the polymorphic transformation of PbO tetragonal (litharge) to PbO orthorhombic (massicot) were measured at four temperatures between 564 and 590° C. The extent of the L → M transformation as a function of time is shown in Fig. 1. The kinetic data [10] were examined by means of a total of nine rate expressions – first order law, Avrami–Erofeev mechanisms, contracting circle and sphere models, and diffusion equations. The most satisfactory kinetic rate laws suggest a diffusion mechanism which is best described in terms of the Jander equation (see Fig. 2). The resultant activation energy was about 130 kcal mol^{-1}.

3.2. Non-isothermal kinetics

The transformation of litharge (red form of PbO) into massicot (yellow form) is characterized by a

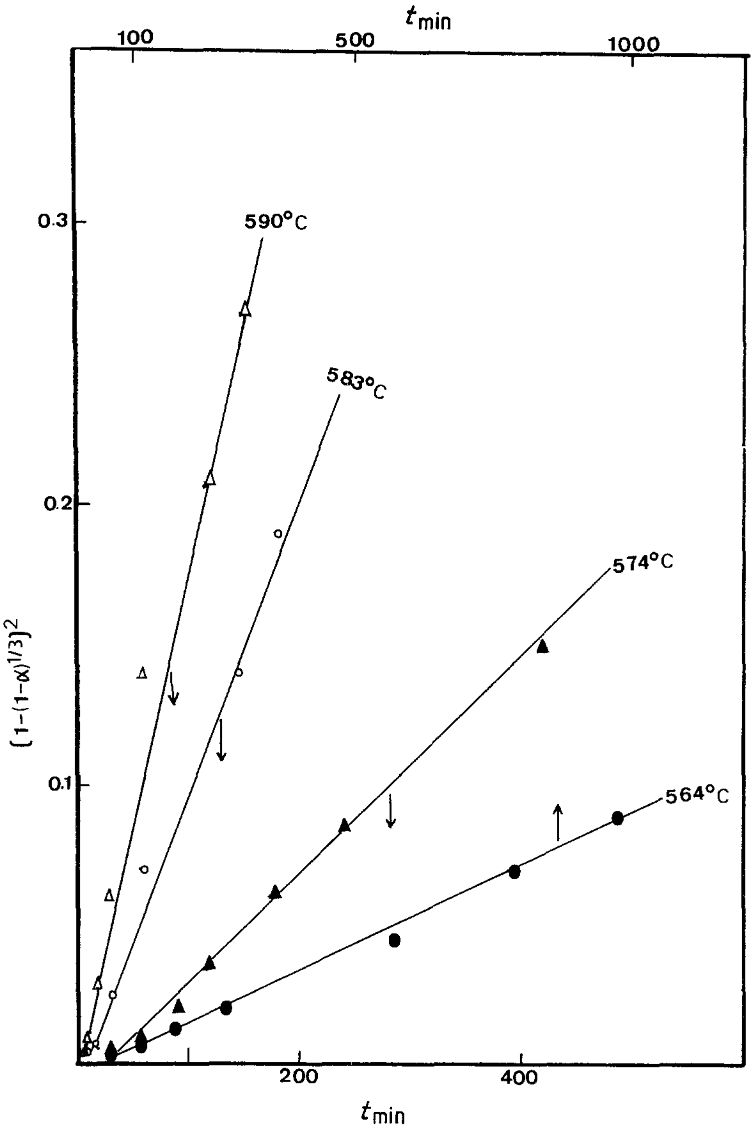

Figure 2 Jander plots of the litharge → massicot transformation data.

weak endothermic effect in the range 580 to 641° C when the DTA curve is recorded at a heating rate of $2°\,\text{C}\,\text{min}^{-1}$. Similar thermal behaviour was observed for the A → C transformation, although the endothermic peak appeared at lower temperatures (see Fig. 3).

According to Marotta *et al.* [1–5], the following two equations can be used for evaluation of the kinetic parameters by means of the DTA technique:

$$\ln \Delta T = -E'/RT + \text{const} \qquad (1)$$

$$\ln h = -E/R\,T_{\text{m}} + \text{const} \qquad (2)$$

where h is the heating rate; ΔT and T_{m} the deflection and the peak temperature of the DTA curve, respectively; E the activation energy and $E' = nE$, where n is a constant related to the growth of nuclei. Recently, Criado and Ortega [16] have demonstrated that E and E' are identical parameters. In fact, Equations 1 and 2 are based upon the assumptions of Piloyan *et al.* [7] and Kissinger [17], respectively.

The plots of $\ln h$ against $1/T_{\text{m}}$ for the A → C and L → M transformations are shown in Fig. 4. Although a straight line is obtained for the A → C transition (correlation coefficient is 0.996), the value of the activation energy calculated from the slope, $60\,\text{kcal}\,\text{mol}^{-1}$, seems meaningless on the basis of the isothermal kinetic analysis. Worse results are obtained for the L → M phase transition. The plot, Fig. 4, gives only a correlation coefficient of 0.978, and an activation energy of

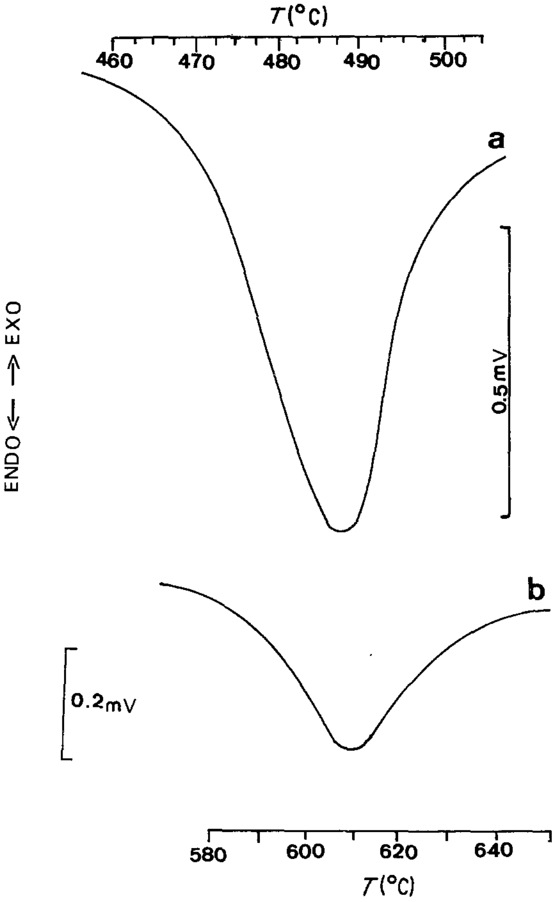

Figure 3 DTA traces: Curve a – aragonite, $h = 10°$ C min^{-1}; Curve b – litharge, $h = 5°$ C min^{-1}.

94 kcal mol^{-1} is obtained. In this respect, Reed *et al.* [18] have pointed out that the Kissinger method can lead to serious errors since the maximum rate of reaction does not coincide with the peak temperature.

Values of ln ΔT taken from curves a and b in Fig. 3 are plotted against $1/T$ in Fig. 5. These plots clearly show poor fitting of the data in Equation 1 (correlation coefficients are 0.928 and 0.976 for aragonite and litharge, respectively). It seems unlikely that the activation energies obtained from the slopes of these plots are meaningful, since in each plot great deviation from the straight line is observed.

Equation 1 is derived from the expression:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{h} f(\alpha) \exp(-E/RT) \qquad (3)$$

taking into account the assumptions of Piloyan *et al.* [7] and Sestak [19], who consider the rate of reaction, $\mathrm{d}\alpha/\mathrm{d}T$, to be proportional to the ΔT deflection from the base line, and that the increase in temperature has a much larger effect on the change in ΔT compared with the change in $f(\alpha)$.

If the second simplification of constant $\ln f(\alpha)$ throughout the reaction is overlooked, the values of the kinetic parameters of the reaction can be calculated from the DTA curves by using Equation 3 written as follows:

$$\ln(\Delta T/f(\alpha)) = \ln(A/h) - E/RT \qquad (4)$$

The degree of conversion, α, was computed from curves a and b in Fig. 3, according to the approximation $\alpha = s/S$, where s is the area swept by the curve at time t and S is the total peak area. The curves representing α against T, derived according to this procedure, are shown in Fig. 6.

The plots of ln $\Delta T/f(\alpha)$ against $1/T$ are shown in Fig. 7. The function $f(\alpha)$ was selected by considering the rate laws compatible with the data obtained under isothermal conditions. Thus, for the A → C transformation – first order law – $f(\alpha) = (1 - \alpha)$, and for the L → M transformation – Jander equation – $f(\alpha) = 3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$. Although Equation 4 led to better correlation coefficients than Equation 1 (Fig. 7) (correlation coefficients of 0.988 and 0.990 for $CaCO_3$ and PbO transformations, respectively), the activation energies calculated from the slopes of the lines obtained by using the least squares method, 179 and 306 kcal mol^{-1} for the A → C and L → M transformations respectively, are larger than those obtained from isothermal experiments.

The results described above give rise to serious doubts about the applicability of the Piloyan and related thermal methods for obtaining the kinetic parameters of phase transitions and similar processes such as the glass-to-crystal transition. The accuracy of the Arrhenius activation energy computed from these methods must be taken with some reservations due probably to the arbitrary assumption of considering the height of the signal curve, ΔT, simply to be directly proportional to the rate of reaction. Furthermore, a significant difference with increasing temperature is observed between the value of the extent of PbO transformation calculated from the area of the peak, and that revealed by powder X-ray diffraction methods (see Fig. 6). To obtain the percentage of conversion by this technique, the DTA experiment was halted at the temperature indicated. The sample was quickly removed and quenched to stop the transformation. In addition, the mixture of red

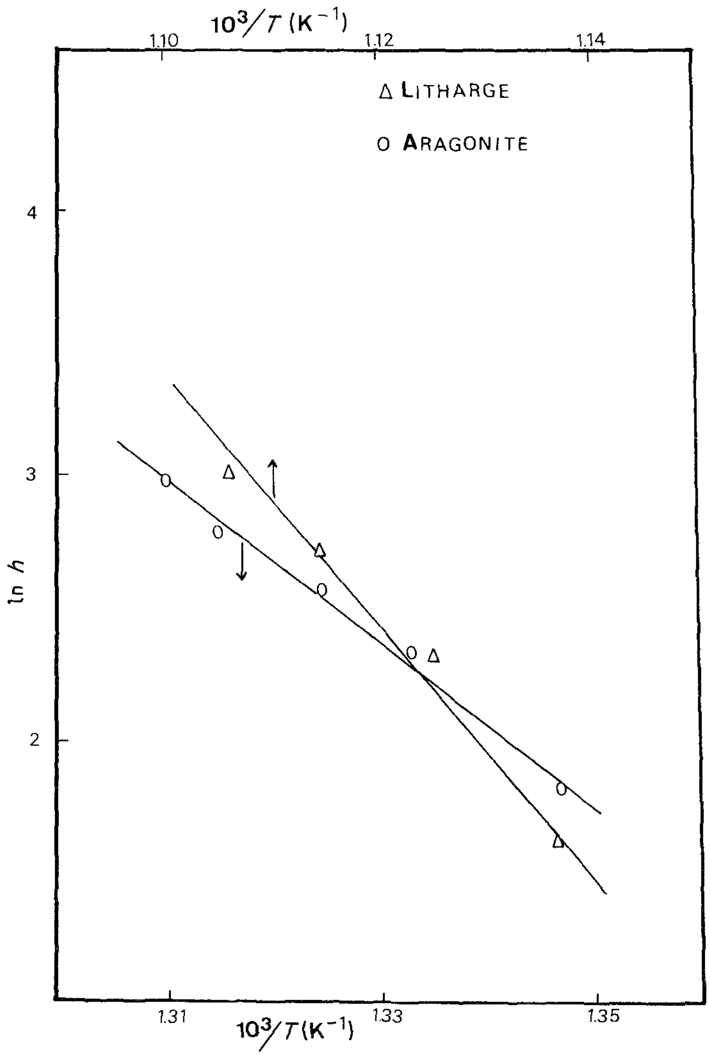

Figure 4 Plots of ln h against $1/T_m$. (The values of peak temperatures have been taken from DTA curves recorded at different heating rates.)

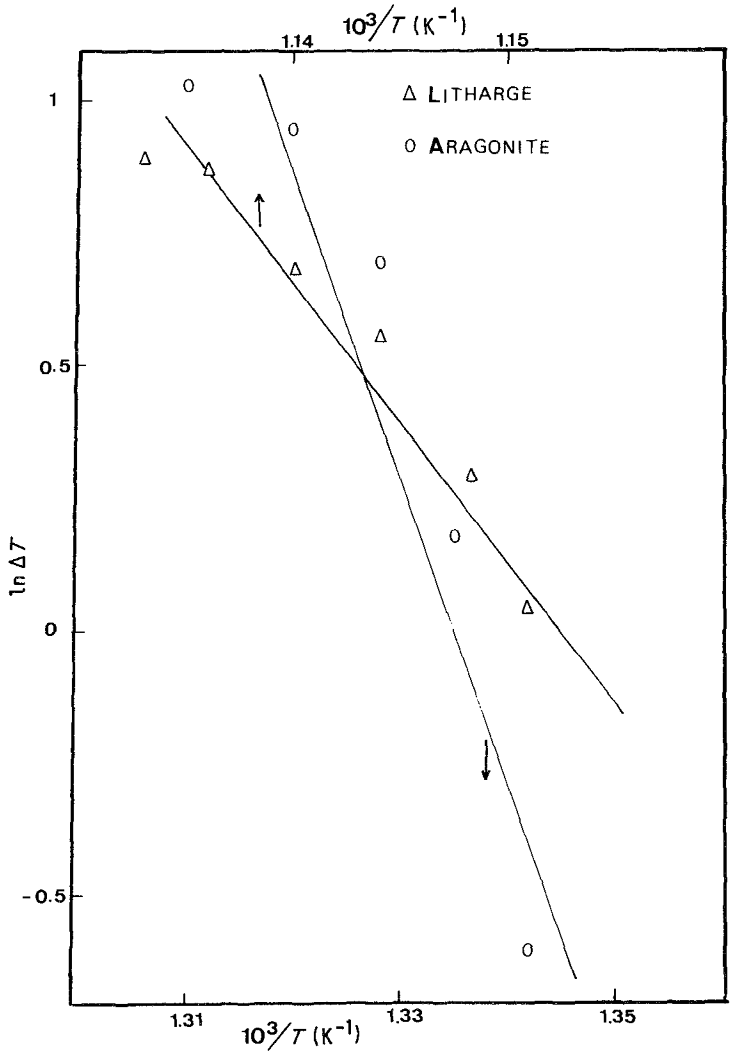

Figure 5 Plots for determination of activation energy according to Piloyan's method (Equation 1).

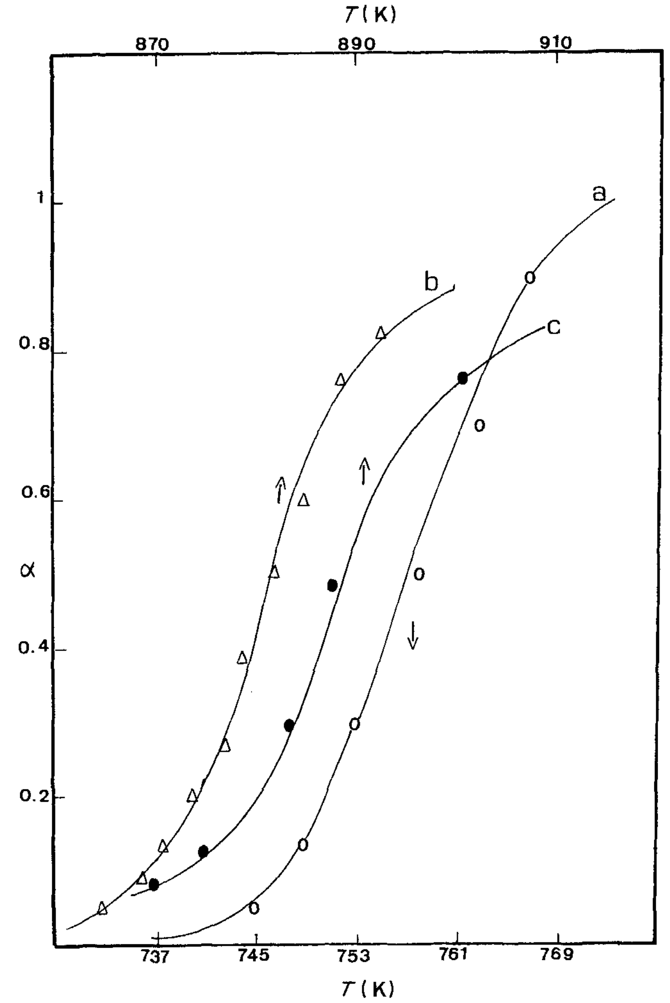

Figure 6 Plots of α against T. Curve a – aragonite; Curves b and c – litharge. (Curves a and b were derived from area measurements of curves in Fig. 3, points of Curve c were obtained from powder X-ray diffraction data of samples prepared by interrupting the DTA experiment.)

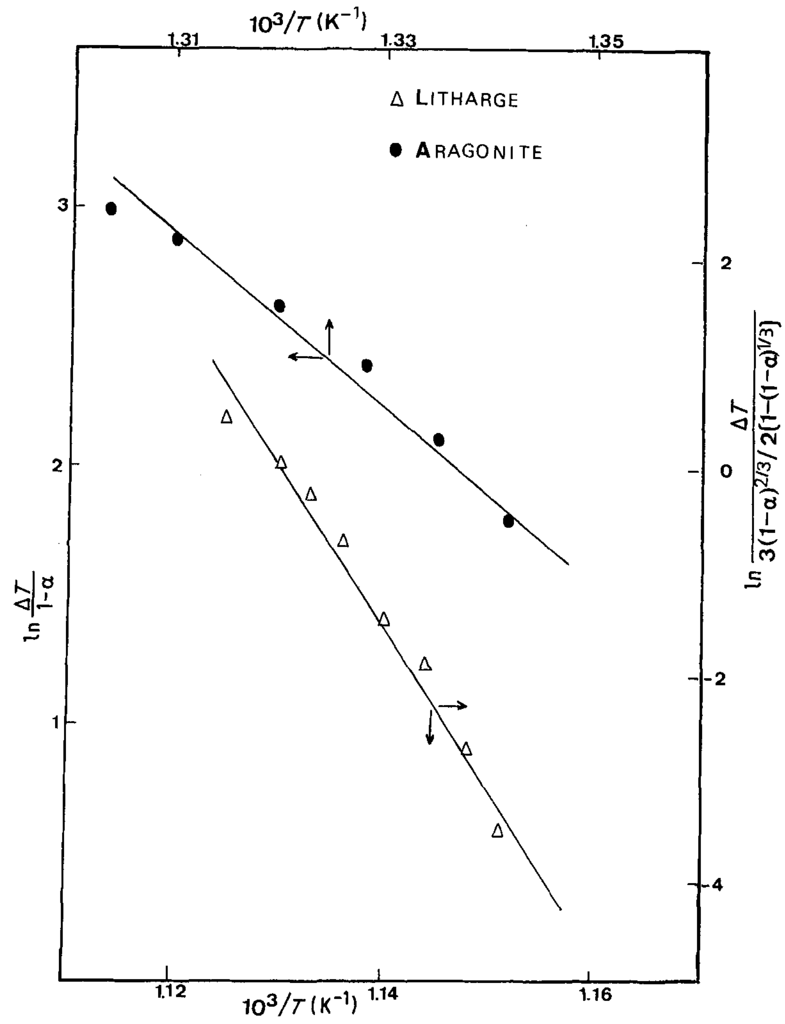

Figure 7 Kinetic analysis of the DTA curves in Fig. 3 according to Equation 4.

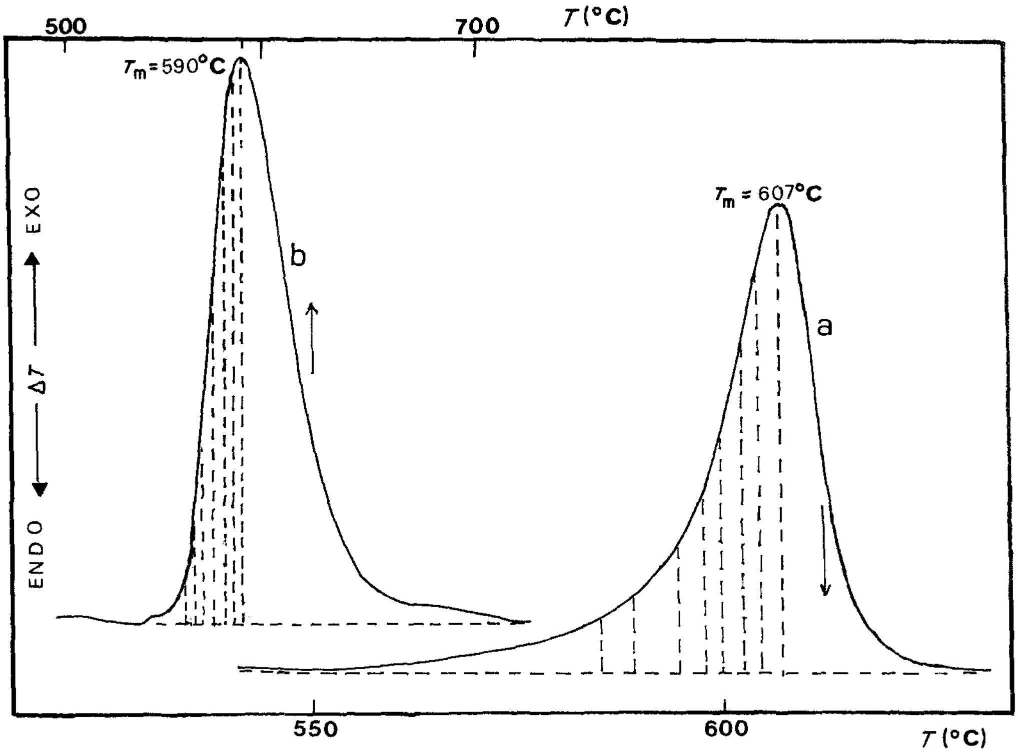

Figure 8 Crystallization peak of $Li_20.2SiO_2$ glass detected by DTA. Curves a and b were taken from [3] and [2], respectively, and amplified with a Rank Xerox 2080.

and yellow colour exhibited by the sample at the end of the endothermic effect clearly demonstrated that a small amount of litharge was not transformed into massicot.

In reviewing the papers of Marotta *et al.* [2, 3] we have observed a change in the form of the crystallization peak of $Li_2O.2SiO_2$ glass detected by DTA, due probably to different heating rates used for recording the curves (see Fig. 8). When the heating rate is higher (the peak temperature T_m is displaced to a higher value), the crystallization takes place with a slow induction period that gives rise to the asymmetric form of the peak (Curve a in Fig. 8). On the other hand, the induction period of Curve b is almost negligible and the crystallization rate increases rapidly with temperature.

According to these observations it would be worth including a re-analysis of these published data by applying Equation 1.

A linear relationship of ln ΔT against $1/T$, Fig. 9, was only obtained for the points of Curve a (correlation coefficient of the straight line being 0.997). The slope of the line was − 77, which gives an activation energy of 154 kcal mol^{-1}.

However, a significant change was observed in the analysis of Curve b, where a poor fitting of the data to Equation 1 becomes apparent. These results do not agree with those reported by Marotta *et al.* [2], since they obtained a straight line for the plot of ln ΔT against $1/T$, and a value of 114 kcal mol^{-1} was calculated for the activation energy from its slope. However, great caution must be taken with the results of Marotta *et al.* [2], since the deflection temperature ΔT is directly proportional to the temperature (see Curve b in Fig. 8). No attempts were made to calculate the apparent activation energy by the root-mean-square regression analysis owing to its value clearly depending on the number of points used in the analysis (Curve b in Fig. 9).

Thus, a variable such as the heating rate alters the appearance of a DTA curve, which results in a difference activation energy calculated by applying Equation 1.

4. Conclusions

The values of activation energy of $CaCo_3$ and PbO transformations obtained from isothermal and non-isothermal methods are summarized in

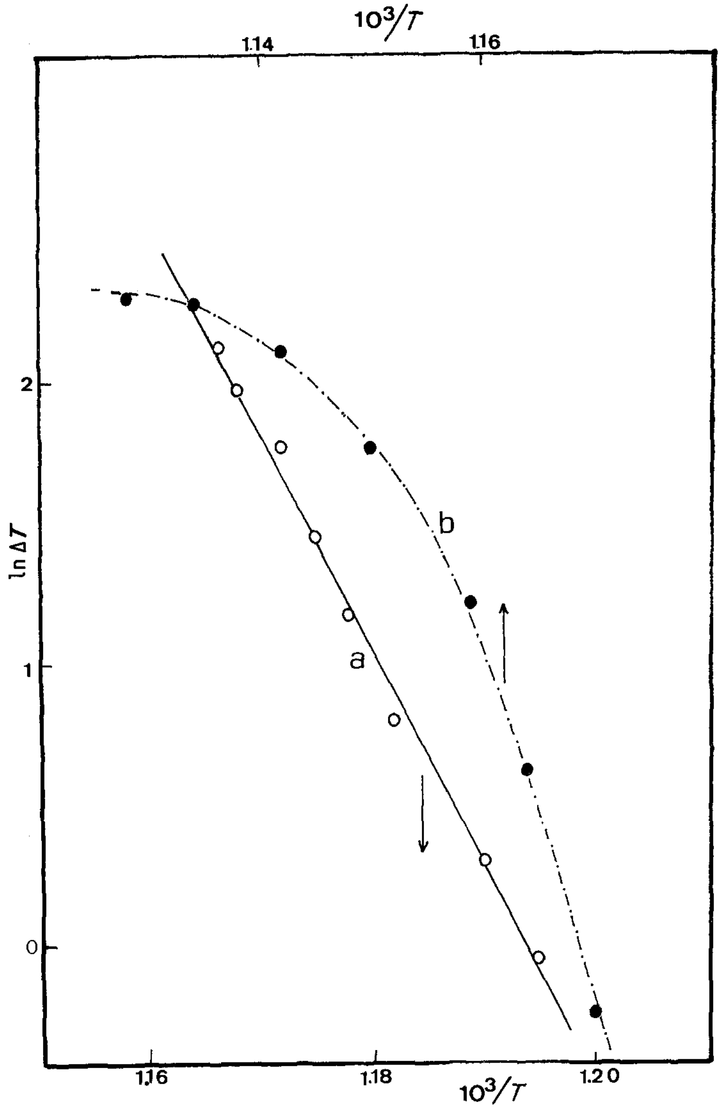

Figure 9 Plot of $\ln \Delta T$ against $1/T$. The values of ΔT and T were taken from the corresponding curves in Fig. 8. (The points used are shown in dotted lines.)

Table I. From these results and taking into account poor fitting of non-isothermal equations and also the discrepancies described in the analysis of the crystallization peak of $Li_20.2SiO_2$ glass, it can be concluded that the methods of obtaining kinetic parameters from DTA curves proposed by Marotta *et al.* [1–5] should be revised, at least in certain cases, due to possible inherent errors of the simplifications employed to derive the equations.

The difficulties in obtaining unambiguously evaluable kinetic results from DTA are related to both experimental and theoretical aspects. The physical assumptions are questionable in some cases and the shape of the DTA curve is determined not only by the kinetic characteristics of the reaction but can be modified by different experimental conditions. In our opinion, further investigations and a new theoretical basis, perhaps as suggested by Meisel [20] irreversible thermodynamics, are needed to extend the application of DTA to kinetic studies of solid-state reactions.

TABLE I Activation energies for aragonite → calcite and litharge → massicot phase transitions (kcal mol^{-1})

Sample	Isothermal	Piloyan method	Kissinger method	Equation 4
Aragonite	134	92	60	179
Litharge	130	92	94	306

References

1. A. MAROTTA, A. BURI and G. L. VALENTI, *J. Mater. Sci.* **13** (1978) 2483.
2. A. MAROTTA and A. BURI, *Thermochim. Acta* **25** (1978) 155.
3. A. MAROTTA, A. BURI and F. BRANDA, *J. Mater. Sci.* **16** (1981) 341.
4. *Idem, J. Therm. Anal.* **21** (1981) 227.
5. A. MAROTTA, S. SAIELLO, F. BRANDA and A. BURI, *J. Mater. Sci.* **17** (1982) 105.
6. M. LASOCKA, *ibid.* **13** (1978) 2055.
7. G. O. PILOYAN, J. D. RYABCHIKOV and O. S. NOVIKOVA, *Nature* **212** (1966) 1229.
8. M. SOPICKA-LIZER and S. PAWLOWSKI, *Thermochim. Acta* **38** (1980) 293.
9. J. MORALES, L. HERNAN, L. V. FLORES and A. ORTEGA, *J. Therm. Anal.* **24** (1982) 23.
10. J. MORALES and M. MACIAS, unpublished results.
11. M. S. RAO and S. R. YOGANASIMHAN, *Amer. Miner.* **50** (1965) 1489.
12. P. PASCAL, "Nouveau Traité de Chimie Minerale" Vol. 8, (Masson et Cie, Paris, 1963) p. 578.
13. M. S. RAO and A. R. V. MURTHY, *Curr. Sci. India* **41** (1972) 774.
14. M. SENNA and H. KUNO, *J. Amer. Ceram. Soc.* **54** (1974) 259.
15. C. N. R. RAO and J. K. RAO, "Progress in Solid State Chemistry: Phase Transformation in Solids" Vol. 4, edited by H. Reise (Academic Press, Oxford, 1967) p. 131.
16. J. M. CRIADO and A. ORTEGA, *Thermochim. Acta* **46** (1981) 213.
17. H. E. KISSINGER, *Anal. Chem.* **29** (1957) 1702.
18. R. L. REED, L. WEBER and B. S. GOTTFRIED, *Int. Ec. Fundam.* **4** (1965) 38.
19. J. SESTAK, *Phys. Chem. Glasses* **15** (1974) 6.
20. T. MEISEL, *Fresenius Z. Anal. Chem.* **312** (1982) 83.

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