Thermochimica Acta 388 (2002) 115–128

thermochimica acta

www.elsevier.com/locate/tca

Kinetic analyses using simultaneous TG/DSC measurements Part I: decomposition of calcium carbonate in argon

John P. Sanders[a], Patrick K. Gallagher[b,*]

[a]The National Brick Research Center, 100 Clemson Research Boulevard, Anderson, SC 20625, USA
[b]409 South Way Court, Salem, SC 29676-4625, USA

Received 30 July 2001; received in revised form 4 October 2001; accepted 4 October 2001

Abstract

Dynamic kinetic analyses are performed on $CaCO_3$ using simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC) measurements in both wet and dry flowing Ar. Differences in the results are discussed in terms of the property measured and the possible influence of the atmosphere on the structural nature of the solid product, CaO. Although the quality of the DSC results was inferior compared with those based on TG, it is clear that they yield different results in subsequent kinetic analyses using a wide range of numerical methods. The presence of moisture in the atmosphere produced slightly lower values of the Arrhenius parameters with less variation during the course of the reaction. Reservations are described concerning the general interpretation of such results. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: TG/DSC measurements; $CaCO_3$; Arrhenius parameters

---

1. Introduction

Several thermoanalytical techniques are often used to follow the course of solid state reactions. Thermogravimetry (TG) and differential scanning calorimetry (DSC) are the most commonly used techniques. Inherent in such studies is the assumption that the property measured is directly related to the concentration of the product and/or reactant (fraction reacted, α) so that the rate of the specific chemical reaction is determined versus time (isothermal) or temperature (dynamic). The relative sensitivities of the two techniques depend upon the change in mass for the process (or processes) (TG) or the enthalpy of the process (or processes) (DSC).

The thermal decomposition of calcium carbonate, $CaCO_3$ was selected for the initial study to compare results obtained from simultaneous measurements on the same sample by these techniques. It was chosen because of the wealth of prior data and analysis available on the rate of this reaction (see for example, the contiguous series of papers commencing with [1] and the references therein), its technological importance, and the *relatively* simple or straightforward nature of the process as suggested by Eq. (1).

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \tag{1}$$

Admittedly the measurements are complicated by the reversibility of the reaction and its strongly endothermic nature; however, these complications should only add interest to the resulting comparison [2–4].

If the process involves a simple single step as indicated by Eq. (1), then it is reasonable to assume that both the change in mass and the heat adsorbed are

---

[*] Corresponding author. Tel.: +1-864-944-6464;
fax: +1-864-656-1095.
E-mail address: P_gallag@bellsouth.net (P.K. Gallagher).

PII: S0040-6031(02)00032-1

a direct indication of α. If, however, the reaction involves formation of an intermediate having a significant lifetime, such as amorphous or microcrystalline $CaCO_3$, then the course of the reaction as followed by each technique will appear differently. The TG measurement would follow only the decomposition or evolution of CO_2 to form the intermediate, while the DSC measurement would follow the weighted sum of the decomposition and the subsequent amorphous to crystalline transition of the intermediate. The weighting factors would depend on the change in enthalpy for each step.

The atmosphere was varied to extend the likelihood of detecting differences between the TG and DSC results. Argon was selected because of its inert nature and because the atomic mass is close to that of the product gas, thus, facilitating mixing and minimizing changes in the thermal conductivity of the atmosphere. Water vapor is known to strongly influence the surface diffusion of the solid product and, therefore, will affect the particle growth and pore structure [5]. This should facilitate any amorphous to crystalline transition in the product. Any $Ca(OH)_2$ formed during heating prior to decomposition of the carbonate should have decomposed to oxide, thus, diluting and diminishing the size of the original sample somewhat, but not entering into the mass loss or adsorption of heat at the decomposition temperature of the carbonate.

2. Experimental procedures

The source of $CaCO_3$ was Mallincrodt analytical reagent grade, which had been heated to a 1000 °C and cooled in a flow of CO_2. Two series of experiments were performed using 29.3 ± 1.3 and 5 ± 0.2 mg sample sizes. The CO_2, 99.5%, and Ar, 99.99%, were from Holox. For selected experiments, the Ar was saturated with water vapor at room temperature prior to entering the instrument. High purity (99.997%) Al foil from AESAR was used for calibration.

Simultaneous TG/DSC was performed using a Netzsch Model 449C instrument with its high temperature furnace. Samples were contained in the manufacturer's Pt crucibles having alumina liners. A 5 mg sample of Al was run at 8 $^\circ C\ min^{-1}$ in dry Ar to determine the correction constants used in the kinetic analysis. The alumina liners were required for the melting of the aluminum. Samples were heated at 25 $^\circ C\ min^{-1}$ to 500 °C and then at selected controlled rates to 1200 °C. The wet or dry Ar flowed over the sample at 0.070 $l\ min^{-1}$. Both TG and DSC baselines were corrected by subtraction of predetermined baselines run under identical conditions except for the absence of sample. A separate heat-flux calibration was performed using a sapphire disk for each heating rate. Six heating rates, 1, 2, 4, 8, 16, and 32 $^\circ C\ min^{-1}$ were performed for the larger sample size and five heating rates, 2, 4, 8, 16, 32 $^\circ C\ min^{-1}$ for the smaller sample size.

The Netzsch Proteus and Thermokinetics software packages were used for data analysis [6]. In the least squares fitting during the kinetic analysis of the TG data no weighting factors were applied to the data. For the DSC measurements tangential baselines and weighting factors of $1/(Y_{max}^2 + Y_{min}^2)$ were applied to the data. The weighing factors are used in cases were the signal is proportional to the heating rate such as DSC measurements so that all of the data receives equal weighing. Instrumental correction factors determined by the software, using the curve for the melting of Al, were factored into the DSC kinetic analysis. These correction factors are used where the measurement itself causes some distortion of the signal. These correction factors are for desmearing functions and thermal resistance corrections. Sources of this distortion relate to thermal transport properties of the crucible and measuring head materials and configuration [7].

3. Results

As a general indication of the raw data, Figs. 1 and 2 present representative plots, using the smaller sample size and intermediate heating rate of 16 $^\circ C\ min^{-1}$, for wet and dry atmospheres, respectively. Fig. 3 presents the curves for the larger sample size at the same heating rate in dry Ar. Tables 1 and 2 summarize some general characteristics for the curves with small and large samples, respectively.

The Thermokinetics software package has the capability to perform three types of model-free kinetic analysis based on the ASTM, Friedman, and Flynn–Ozawa approaches. All three methods were utilized with the four sets of data summarized in Tables 1 and 2

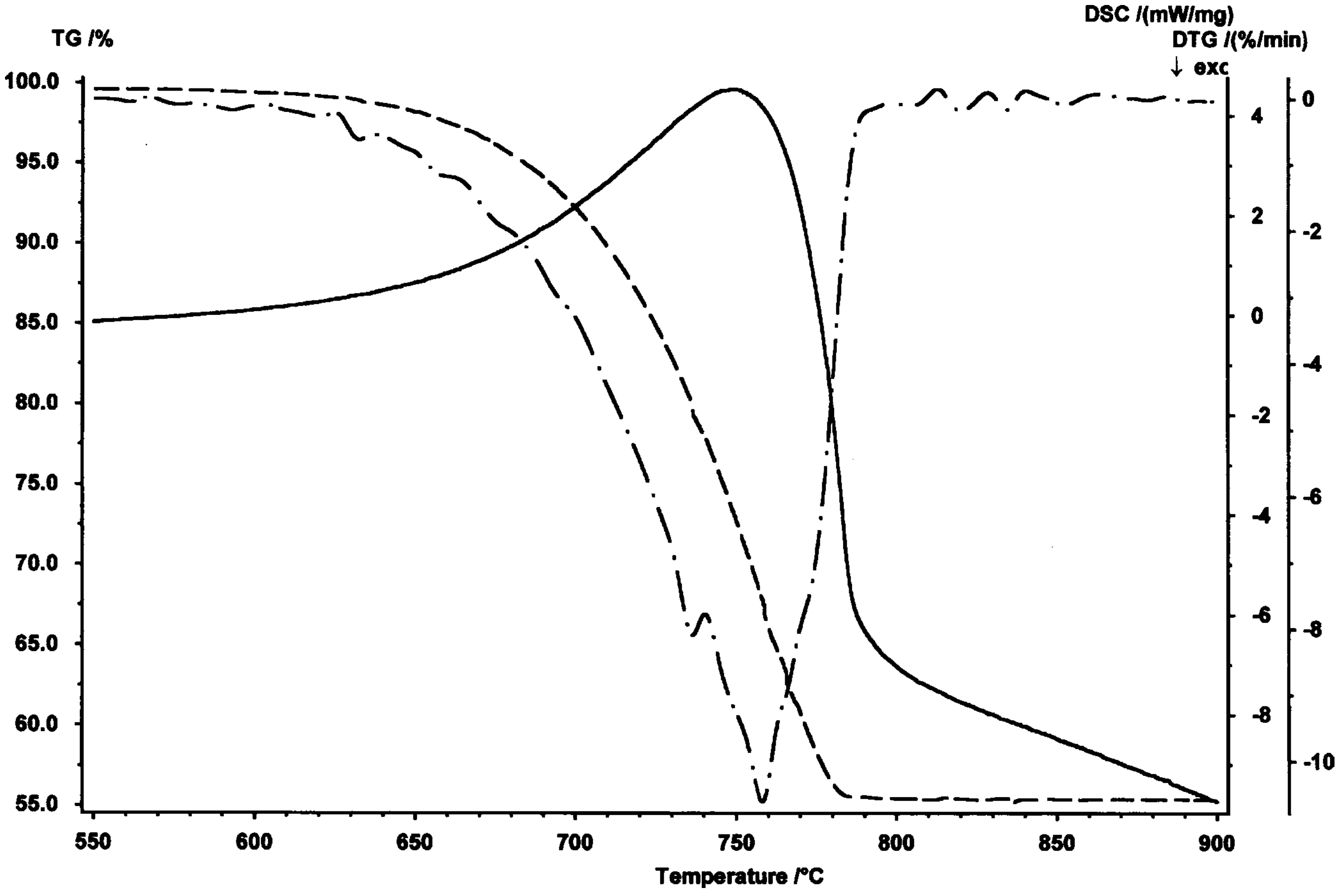

Fig. 1. Curves for the simultaneous TG/DSC of 5.0 mg of $CaCO_3$ heated at 16 °C min^{-1} in dry Ar: (—) DSC; (- - -) TG; (-·-·-) DTG.

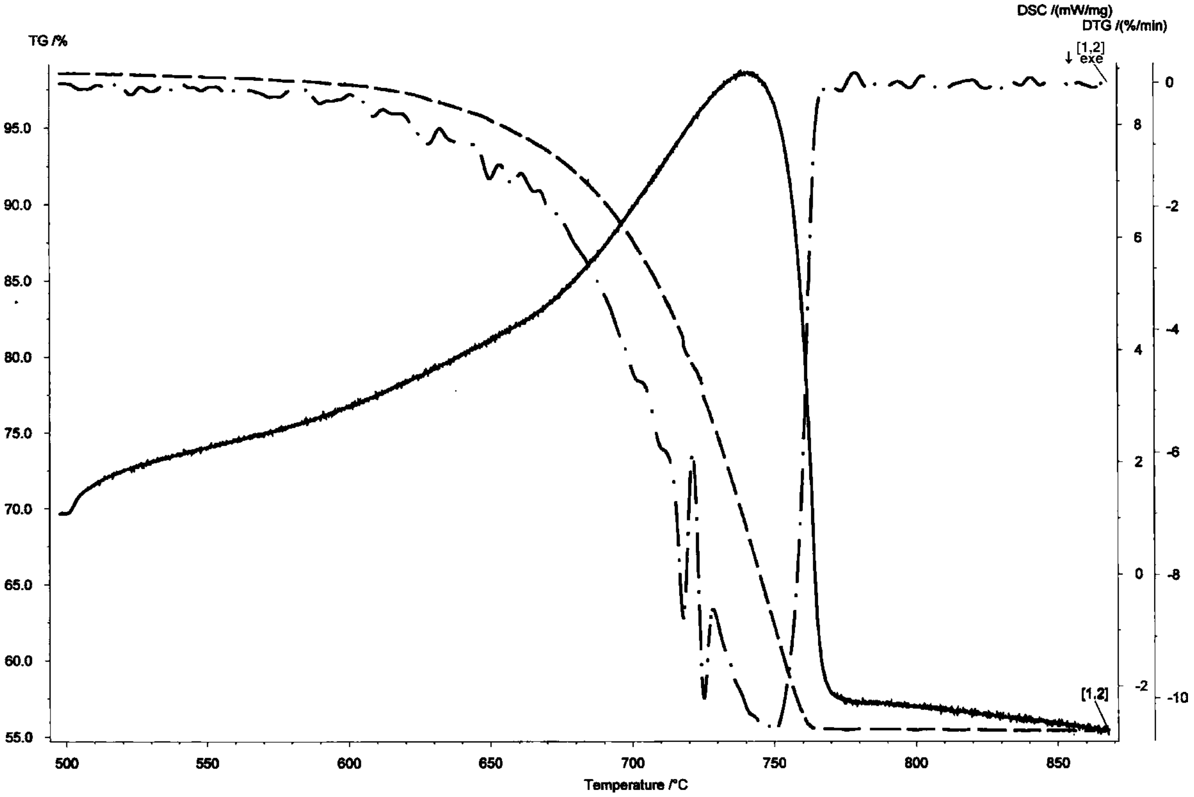

Fig. 2. Curves for the simultaneous TG/DSC of 4.9 mg of $CaCO_3$ heated at 16 °C min^{-1} in wet Ar: (—) DSC; (- - -) TG; (-·-·-) DTG.

and the data from the study by ICTAC [1]. Figs. 4 and 5 show representative sets of curves after transfer to and preparation for kinetic analysis for TG and DSC data, respectively.

Fig. 6 and Table 3 present the results of the ASTM-based analysis. Table 4 summarizes the range of activation energies, E_a and pre-exponential terms, $\log A$, obtained for each data set using the Friedman analysis. Figs. 7 and 8 show the variation of E_a and $\log A$ as a function of α from the Flynn–Ozawa analysis using TG data for the smaller sample size in dry and wet atmospheres, respectively. The results from the Flynn–Ozawa are summarized in Table 5.

The linear regression section of the kinetic analysis software allows one to fit the usual selection of kinetic models over whatever range of α one chooses. A range

Table 1
Selected values for the simultaneous TG/DSC of 5 mg samples of $CaCO_3$ heated in Ar

Heating rate (°C/min)	Dry Argon			Wet Argon		
	Sample mass (mg)	DTG T_{max} (°C)	DSC T_{max} (°C)	Sample mass (mg)	DTG T_{max} (°C)	DSC T_{max} (°C)
2	5.1	677	658	5.1	668.4	642.9
4	5.1	706	680	5.2	696.1	674.0
8	5.2	732	720	5.0	720.5	709.5
16	5.0	758	750	5.2	750.1	741.1
32	5.2	785	790	5.0	779.3	777.4

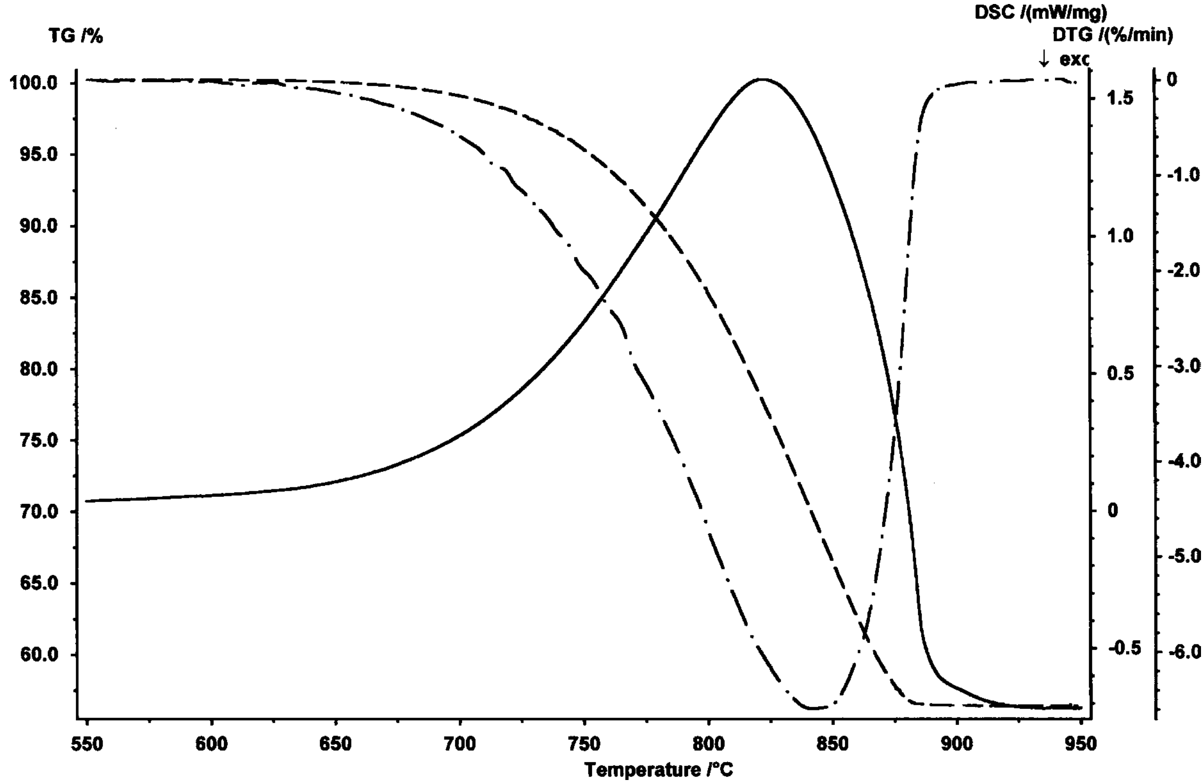

Fig. 3. Curves for the simultaneous TG/DSC of 30.5 mg of $CaCO_3$ heated at 16 °C min^{-1} in dry Ar: (—) DSC; (- - -) TG; (-·-·-) DTG.

of $0.01 > \alpha > 0.99$ was selected. Tables 6 and 7 present the results for small and large sample sizes, respectively, using the best fitting model.

Non-linear regression allows a wide selection of consecutive and competing models to be selected, with a choice of the range in α to be considered. Reasonable selections were made for a two-step consecutive process, using insight derived from the linear regression results presented in Tables 6 and 7. The range of a used was the same as for the other analyses. Tables 8 and 9 summarize the results for the best fitting model for the small and large sample sizes, respectively. The degree of fit to the TG and DSC data is indicated in Figs. 9 and 10, respectively, for the analyses using the smaller sample size heated in dry Ar, see Table 8.

Table 2
Selected values for the simultaneous TG/DSC of 29.3 mg samples of $CaCO_3$ heated in dry Ar

Heating rate (°C/min)	Sample mass (mg)	DTG T_{max} (°C)	DSC T_{max} (°C)
1	29.4	703	680
2	28.4	724	708
4	29.6	776	756
8	28.3	807	788
16	30.5	828	807
32	30.5	891	862

Data from the kinetic study by ICTAC.

4. Discussion

Several relevant generalizations should be noted based on inspection of Figs. 4 and 5 and Tables 1 and 2. There is the natural progression to higher apparent temperatures of reaction with increasing heating rate and sample size. The effect of heating rate is greater for the larger sample size. With only one exception, the peak temperature of the DSC curve is at a lower temperature than for the corresponding DTG

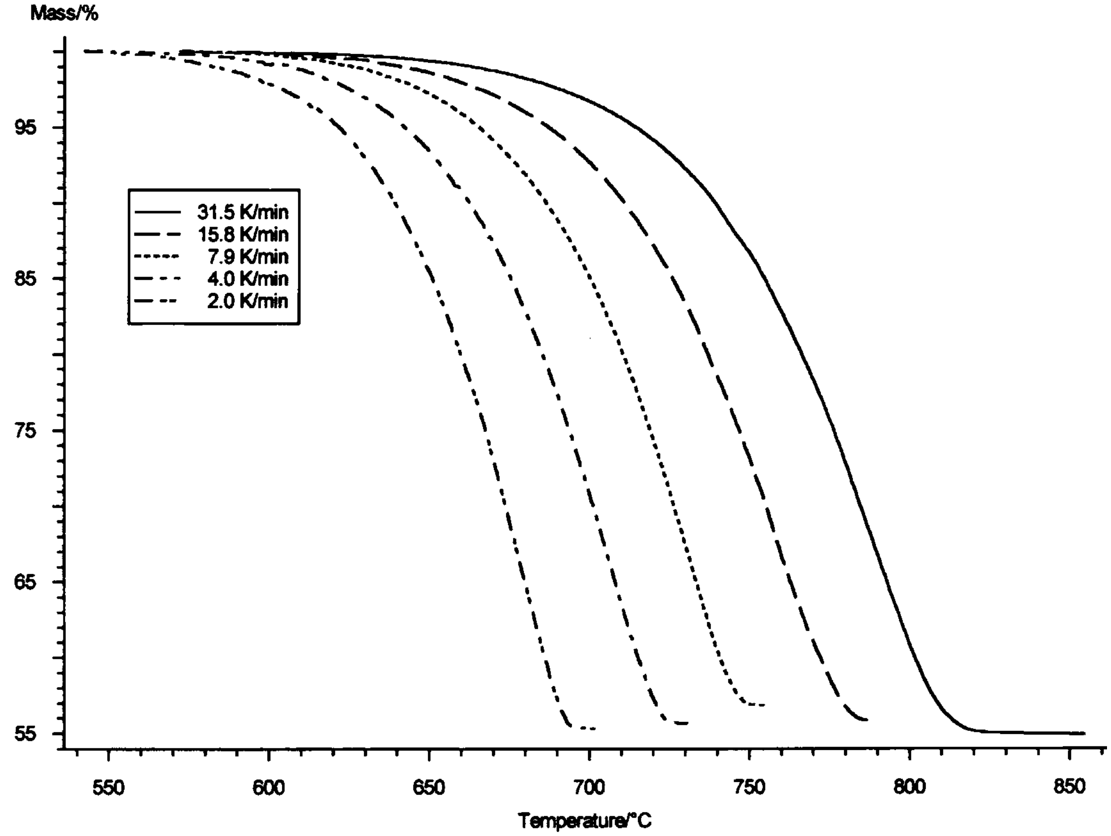

Fig. 4. Adjusted TG curves for the thermal decomposition of $CaCO_3$ prior to kinetic analysis for the smaller sample size heated in dry Ar.

curve (see Figs. 1–3). This difference is greater at slower heating rates for the smaller sample size, but remains relatively constant for the larger samples. The decomposition in wet Ar takes place at slightly lower temperatures, and in a shorter period of time, than in a dry atmosphere.

The amplitude of the DSC peak decreases with decreasing heating rate and consequently the baseline becomes much more difficult to establish. There is also a pronounced change in heat capacity associated with the loss of CO_2, leading to a severe step in the baseline, further complicating its establishment. The

Table 3
Selected results from the ASTM model-free kinetic analysis for the decomposition of $CaCO_3$

Sample size	Atmosphere	Technique	E_a (kJ/mol)	Log A (s^{-1})
Small	Dry Ar	TG	204 ± 8	8.30
Small	Dry Ar	DSC	213 ± 11	8.79
Small	Wet Ar	TG	183 ± 6	7.33
Small	Wet Ar	DSC	193 ± 4	7.82
Large	Dry Ar	TG	156 ± 7	5.08
Large	Dry Ar	DSC	213 ± 25	8.03
ICTAC[a]	Dry N_2	TG	191 ± 10	7.02
ICTAC[a]	Vacuum	TG	117 ± 13	4.21

[a] Data from the kinetic study by ICTAC.

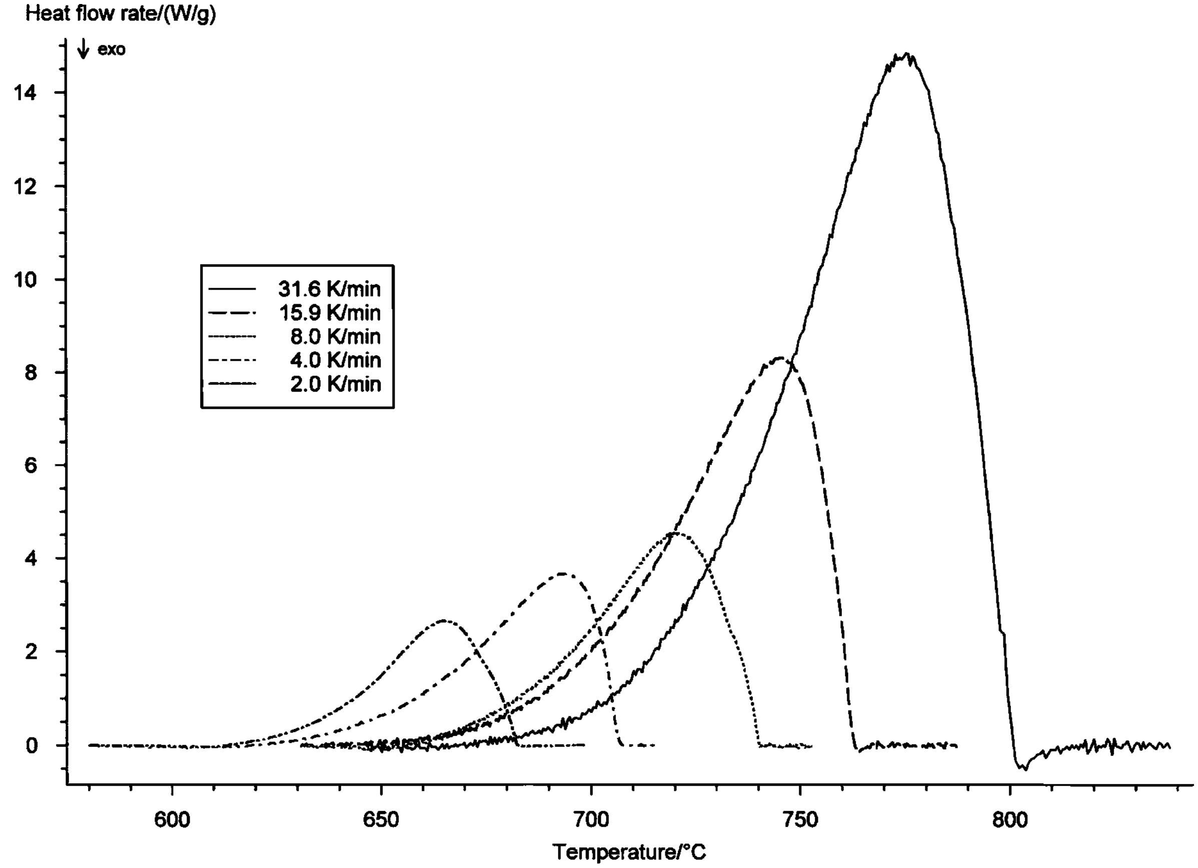

Fig. 5. Adjusted DSC curves for the thermal decomposition of $CaCO_3$ prior to kinetic analysis for the smaller sample size heated in wet Ar.

resulting areas are very dependent on this choice of baseline and little significance is assigned to absolute values of the resulting areas. It was noted, however, that the apparent values of ΔH from the measurements of the smaller samples were generally too large, while those derived from the larger samples were too small, compared to the thermodynamic change in enthalpy of about 1800 J g^{-1}. A kinetic analysis based on fractional areas within the same peak, however, should have greater significance. Inspection of Figs. 2 and 5

Table 4
Selected results from the Friedman model-free kinetic analysis for the decomposition of $CaCO_3$

Sample size	Atmosphere	Technique	E_a (kJ/mol)	Log A (s^{-1})
Small	Dry Ar	TG	223–139	9.1–5.8
Small	Dry Ar	DSC	264–166	11.2–7.3
Small	Wet Ar	TG	205–156	8.4–6.6
Small	Wet Ar	DSC	187–172	8.0–6.5
Large	Dry Ar	TG	184–120	6.2–3.8
Large	Dry Ar	DSC	258–131	9.9–4.9
ICTAC[a]	Dry N_2	TG	183–189	6.3–8.0
ICTAC[a]	Vacuum	TG	94–135	5.0–3.2

[a] Data from the kinetic study by ICTAC.

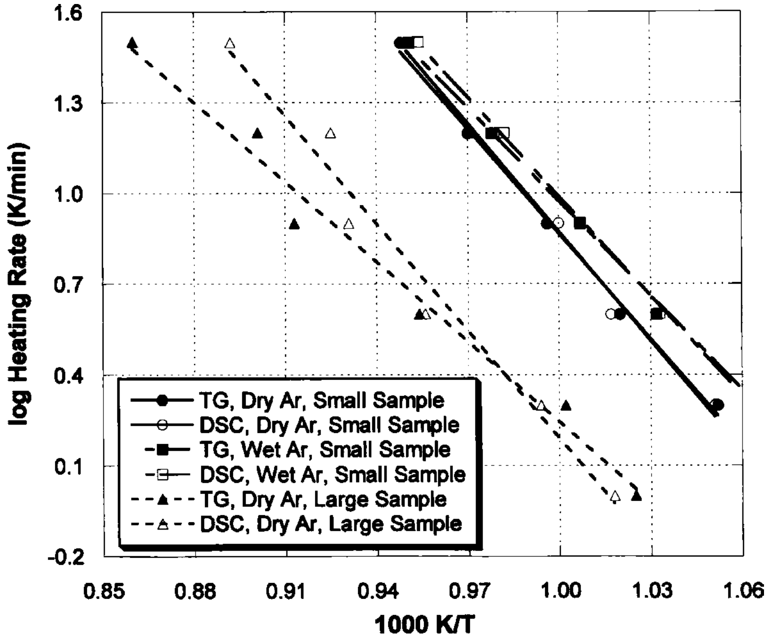

Fig. 6. Plots of the kinetic analysis based on the ASTM method.

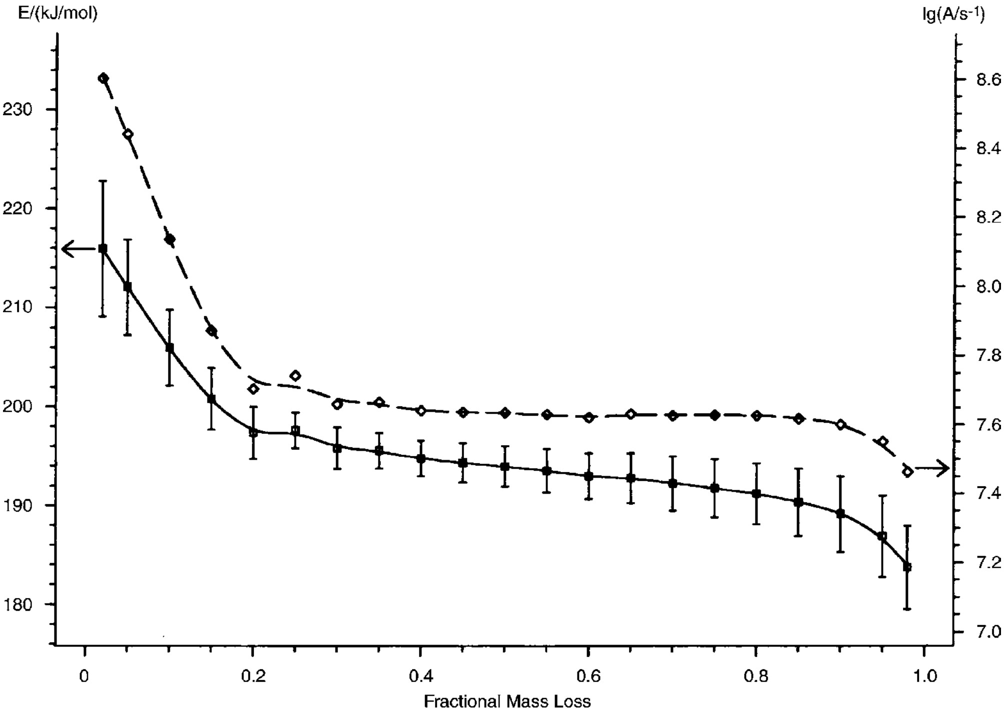

Fig. 7. A plot of E_a and log A as a function of a for the decomposition of the small sample size of $CaCO_3$ in dry Ar based on the Flynn–Ozawa model free method using the TG results.

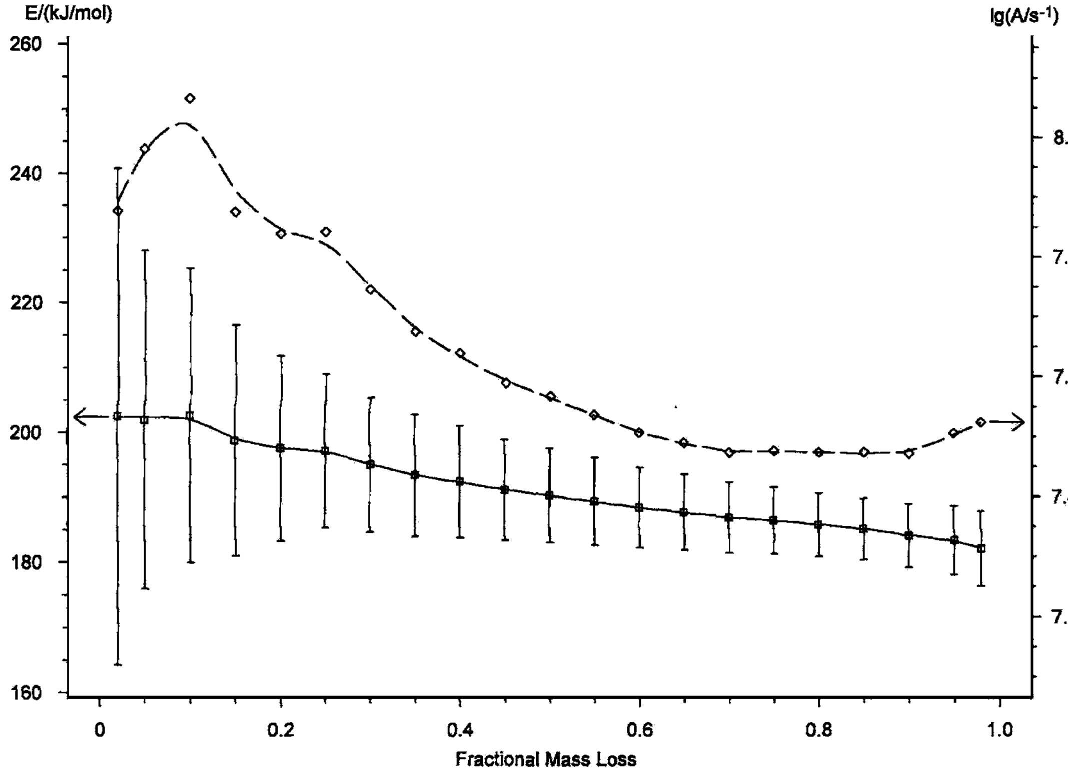

Fig. 8. A plot of E_a and log *A* as a function of a for the decomposition of the small sample size of $CaCO_3$ in wet Ar based on the Flynn–Ozawa model free method using the DSC results.

indicates that the baseline correction utilized in the Thermokinetics software produces a good horizontal baseline.

As the name indicates, the model-free kinetic analyses have the advantage of alleviating the need to select a specific kinetic model and hence any dependence on this choice. Fig. 6 and Table 3 present the results for the ASTM procedure [8]. The results using the dry Ar agree quite well with those derived from the ICTAC data in dry N_2 and have comparable error limits. The values derived from wet data, however, are somewhat lower. This could be attributed to the ability of surface hydroxyl groups to facilitate self-diffusion in the product.

Table 5
Selected results from the Flynn–Ozawa model-free kinetic analysis for the decomposition of $CaCO_3$

Sample size	Atmosphere	Technique	E_a (kJ/mol)	Log *A* (s^{-1})
Small	Dry Ar	TG	218–184	8.7–7.5
Small	Dry Ar	DSC	282–196	12.2–8.1
Small	Wet Ar	TG	203–182	8.1–7.5
Small	Wet Ar	DSC	235–190	9.0–8.0
Large	Dry Ar	TG	182–150	6.0–4.8
Large	Dry Ar	DSC	349–159	14.7–5.5
ICTAC[a]	Dry N_2	TG	220–194	8.2–7.4
ICTAC[a]	Vacuum	TG	162–110	6.3–4.0

[a] Data from the kinetic study by ICTAC.

Table 6
Selected results of the linear regression kinetic analysis for the thermal decomposition of $CaCO_3$ using the smaller sample size and data from ICTAC.

Atmosphere	Technique	Model	Order, n	a or Kcat	E_a (kJ/mol)	Log A (s^{-1})	R^2
Dry Ar	TG	Bna[b]	0.424	0.164	204	7.57	0.9994
Dry Ar	DSC	Cnb[c]	0.672	0.584	207	7.97	0.9885
Wet Ar	TG	Cnb[c]	0.644	0.350	188	7.22	0.9967
Wet Ar	DSC	Bna[b]	0.509	0.544	187	7.73	0.9928
Dry N_2[a]	TG	F_n[d]	0.146	–	193	6.80	0.9935
Vacuum[a]	TG	Bna[b]	0.658	0.317	109	3.91	0.9996

[a] Data from the kinetic study by ICTAC.

[b] Expanded Prout–Tompkins equation $d\alpha/dt = -A\exp(-E_a/RT)(1-\alpha)^n\alpha^a$.

[c] nth-order reaction with autocatalysis $d\alpha/dt = -A\exp(-E_a/RT)((1-\alpha)^n(1+\mathrm{Kcat}\cdot\alpha))$.

[d] nth-order reaction $d\alpha/dt = -A\exp(-E_a/RT)(1-\alpha)^n$.

Table 7
Selected results of the linear regression kinetic analysis for the thermal decomposition of $CaCO_3$ in dry Ar using the larger sample size

Technique	Model	Order	a or Kcat	E_a (kJ/mol)	log A (s^{-1})	R^2
TG	Cnb[a]	1.030	0.574	162	5.01	0.9884
DSC	Bna[b]	0.962	0.436	191	7.06	0.9484

[a] nth-order reaction $d\alpha/dt = -A\exp(-E_a/RT)(1-\alpha)^n$.

[b] Expanded Prout–Tompkins equation $d\alpha/dt = -A\exp(-E_a/RT)(1-\alpha)^n\alpha^a$.

Table 8
Selected results of the non-linear regression kinetic analysis for the thermal decomposition of $CaCO_3$ using the smaller sample size and data from ICTAC

Atmosphere	Technique	Model	Order	a or Kcat	E_a (kJ/mol)	log A (s^{-1})	w[f]	R^2
Dry Ar	TG	1, F_1[b]	1.000	–	265	11.95	0.04	0.9998
		2, F_n[c]	0.268	–	166	6.16		
Dry Ar	DSC	1, Bna[d]	0.395	0.169	227	9.62	0.09	0.9895
		2, F_n[c]	0.464	–	188	7.50		
Wet Ar	TG	1, F_n[c]	0.249	–	176	6.75	0.49	0.9972
		2, F_n[c]	0.870	–	288	13.6		
Wet Ar	DSC	1, Bna[d]	0.294	0.547	194	8.35	0.10	0.9951
		2, F_n[c]	0.621	–	207	9.00		
Dry N_2[a]	TG	1, F_1[b]	1.000	–	135	4.55	0.04	0.9994
		2, F_n[c]	0.161	–	198	7.08		
Vacuum[a]	TG	1, C_1[e]	1.000	0.589	132	5.35	0.17	0.9997
		2, F_n[c]	0.496	–	97	3.06		

[a] Data from the kinetic study by ICTAC.

[b] First-order reaction $d\alpha/dt = -A\exp(-E_a/RT)(1-\alpha)$.

[c] nth-order reaction $d\alpha/dt = -A\exp(-E_a/RT)(1-\alpha)^n$.

[d] Expanded Prout–Tompkins equation $d\alpha/dt = -A\exp(-E_a/RT)(1-\alpha)^n\alpha^a$.

[e] First-order reaction with autocatalysis $d\alpha/dt = -A\exp(-E_a/RT)(1-\alpha)(1+\mathrm{Kcat}\cdot\alpha)$.

[f] Parameter w is the weighting factor used for modeling with consecutive reactions.

Table 9
Selected results of the non-linear regression kinetic analysis for the thermal decomposition of $CaCO_3$ in dry Ar using the larger size

Atmosphere	Technique	Model	Order	a or Kcat	E_a (kJ/mol)	Log A (s^{-1})	w[c]	R^2
Dry Ar	TG	1, F_n[a]	0.392	–	185	6.65	0.26	0.9893
		2, F_n[b]	0.515	–	139	4.18		
Dry Ar	DSC	1, Bna[b]	0.940	0.532	206	8.00	0.05	0.9617
		2, F_n[a]	0.318	–	104	243		

[a] nth-order reaction $d\alpha/dt = -A \exp - E_a/RT(1-\alpha)^n$.

[b] Expanded Prout–Tompkins equation $d\alpha/dt = -A \exp(-E_a/RT)(1-\alpha)^n \alpha^a$.

[c] Parameter w is the weighting factor used for modeling with consecutive reactions.

The Arrhenius parameters derived from the DSC measurements are higher in all cases than those from the TG measurements. The larger sample size and the results for the ICTAC data in vacuum yield lower values. Because the decomposition of the larger sample size has moved to higher temperature, those curves are markedly shifted from the others in Fig. 6. Thermal transport factors would be a greater problem for both of these conditions. Very recent work by Kyobe and Mulokozi substantiate the strong influence of thermal transport on the rate of this reaction and propose a method of analysis to take this influence into account [9].

Other model free analyses are the Friedman and the Flynn–Ozawa methods [10]. The results utilizing

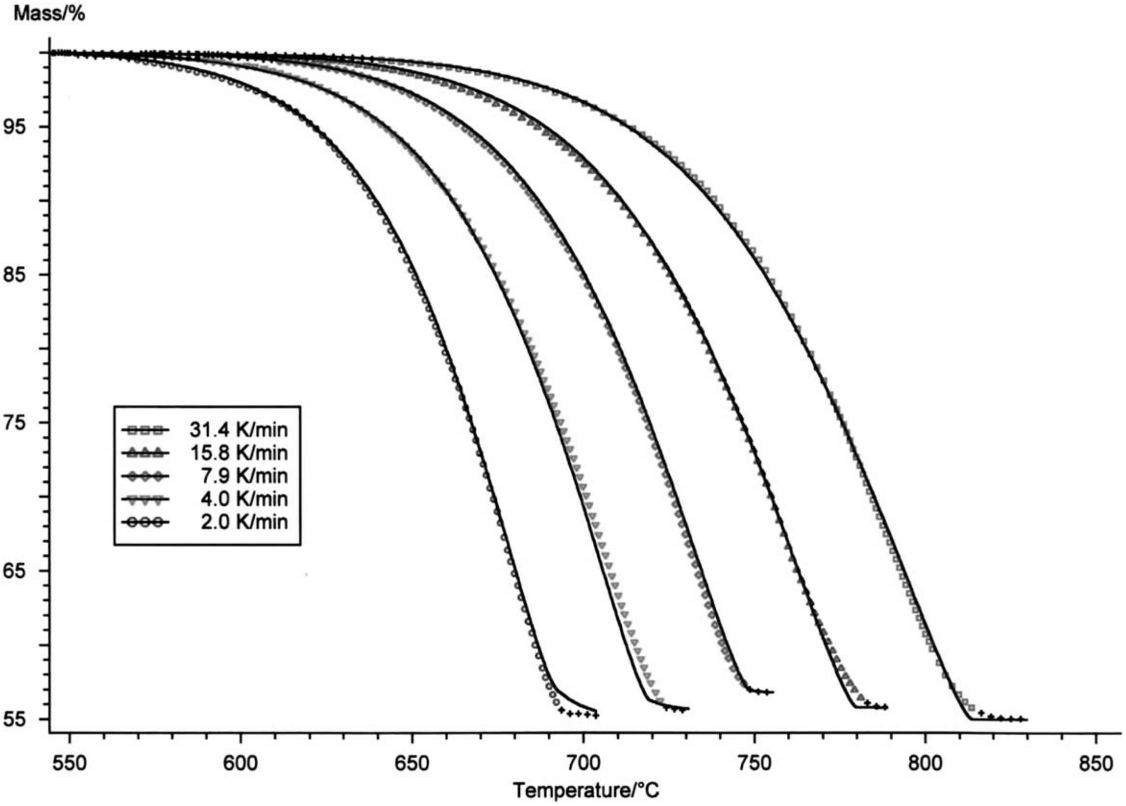

Fig. 9. Indication of fit for the non-linear kinetic analysis of the TG data for the thermal decomposition of $CaCO_3$ in dry Ar using the smaller sample size. See Table 8 for the kinetic models.

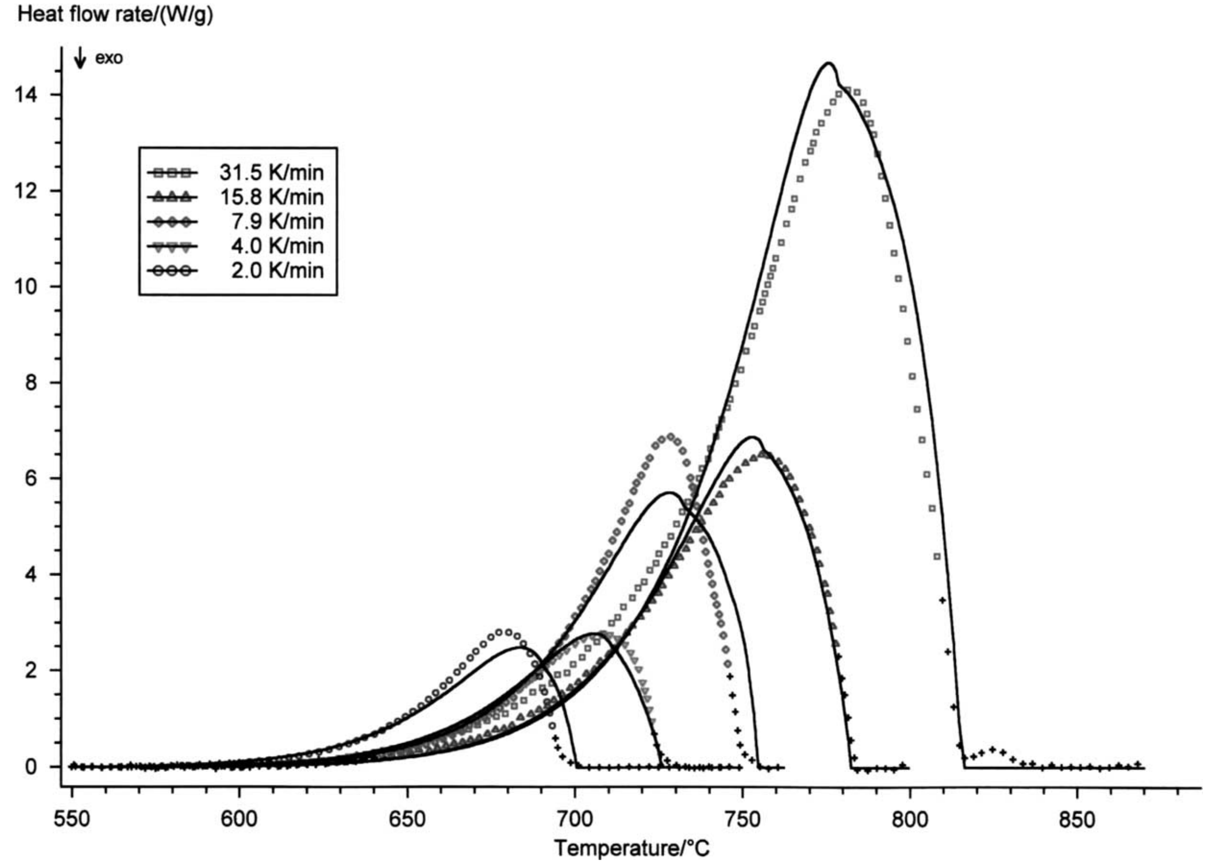

Fig. 10. Indication of fit for the non-linear kinetic analysis of the DSC data for the thermal decomposition of $CaCO_3$ in dry Ar using the smaller sample size. See Table 8 for the kinetic models.

these approaches are presented in Tables 4 and 5 and Figs. 7 and 8. A characteristic of these methods is that they allow the Arrhenius parameters to vary during the course of the reaction, as seen in Figs. 7 and 8. Consequently, the tabulated results indicate a range in values over the course of the reaction. The very close correspondence in the variation of E_a and $\log A$ indicated in both the tables and figures raises serious questions about their independence and, hence, significance of these values in heterogeneous kinetics.

The ill-conditioned mathematical nature of the Arrhenius equation has been noted and discussed many times, see for example and references therein [11–13]. The resulting linear relationship between E_a and $\log A$ is often referred to as an example of ''the kinetic compensation effect''. Consequently, the present authors view these values as merely fitting parameters suitable for predicting rates within the range of temperature and under the experimental conditions used in their derivation. Extrapolation beyond these conditions is questionable. Although there is considerable variation in the model-free results, the singular values derived from the ASTM results fall within the range indicated by the other two analyses and the relationships associated with sample size, TG versus DSC, and wet versus dry are consistent.

A general reservation should be mentioned prior to discussing the linear and non-linear regression analyses based on specific kinetic models. The general approach is to look for a good fit as expressed by the R^2 value from the least squares fitting program applied to the selected models. A compromise must be reached by each investigator concerning the *reasonable* degree of freedom that should be allowed in the analyses.

Clearly the more degrees of freedom or variables introduced into the analysis, the better the resulting R^2. Choosing an *n*th-order model or allowing more parameters into the specific mechanism, e.g. catalytic variances or multiple reaction paths, will always provide a better fit than a specific order or a single reaction. As can be seen in Tables 6 and 7, the authors have allowed the order to vary and the possibility of autocatalysis in the linear regression analyses of the best fitting models offered in the Thermokinetics software package. The best fitting models in Tables 6 and 7 all take advantage of this added freedom. In addition the linear relationship "kinetic compensation effect" between E_a and $\log A$ continues.

Although the best fitting models vary, the Arrhenius parameters for both the TG and DSC data in dry Ar agree very well with each other and are close to those determined for the set of ICTAC data run in dry N_2. The values derived from the measurements in wet Ar and for the larger sample size, however, are lower. These comparisons are the same as those concluded from the model-free analyses.

It is also obvious from the values of R^2 that the DSC data do not fit the analyses as well as the TG data in every instance. This is substantiated by comparison of the fits indicated in Figs. 9 and 10. The inferior quality of the DSC results is most probably due largely to the difficulties associated with the corrections in the baseline that were described earlier in the Section 2. Also, the conditions were not ideal for DSC. The use of open containers with ceramic liners degraded the quality of the DSC data, but were necessary for this study in order to allow for the escape of the product gas and prevent the reaction of the Al standard with the crucible. In addition, the construction of a simultaneous instrument, of necessity, favors less optimum conditions for DSC. The quality of data from TG is far less affected by heating rate and slight disturbances in the local environment, so the better fit is to be expected. The consistently higher values of the Arrhenius parameters, the variance in the best fitting kinetic model, and the differences in peak temperatures noted earlier in Tables 1 and 2, clearly suggest, however, that the two methods are unlikely to yield identical kinetic evaluations or conclusions.

The question posed in the Section 1 concerning the establishment of an intermediate amorphous or microcrystalline product should be best answered by the non-linear regression analysis with consecutive reactions. The premise is that the TG data would not show a significant improvement in the quality of fit, since it is determined solely by the first-stage decomposition reaction. Analyses of the DSC data, on the other hand, should show a marked improvement based on the resolution of the two separate processes.

Unfortunately, several factors preclude a clear solution to this issue. Among these factors are the inferior quality of the DSC measurements and the problems associated with the inability to obtain unique solutions to the Arrhenius equation. Comparison of the values of R^2 between Tables 6 and 8 and Tables 7 and 9 indicates a very small improvement in the fit upon the addition of the added freedom associated with the coupling of a second reaction for either the TG or the DSC analyses. The improvement is so small that the added interpretation seems unwarranted in either case.

5. Conclusions

- Several problems associated with DSC data add substantial uncertainty and tend to lower the quality of DSC results compared to those from TG data in simultaneous measurements.
- Determining unique values of the Arrhenius parameters requires very precise data. Varying E_a associated with a compensating variation in $\log A$ has questionable significance.
- Care should be exercised in fitting kinetic models with increasing degrees of mathematical freedom. Considerable restraint and good judgment are needed in the quest for a better numerical fit to the data.
- In this study, there is reasonable agreement among the various methods of numerical analysis for the TG and DSC data. Results using a small sample mass in dry Ar agree well with prior data from an ICTAC study derived in dry N_2. Results for a larger sample size, however, yield lower values of *both* E_a and $\log A$.
- Water vapor in the atmosphere lowers the resulting values of *both* E_a and $\log A$. The increased rate is attributed to enhanced self-diffusion in the product layer.
- Although the first three points above tend to cloud the issue, it does appear that results derived from TG and DSC data have significant differences. The fact that the DSC and DTG curves are not directly

superimposable also implies the lack of direct correspondence.

References

[1] M.E. Brown, Thermochim. Acta. 355 (2000) 125.

[2] P.K. Gallagher, D.W. Johnson Jr., Thermochim. Acta. 6 (1973) 67.

[3] P.K. Gallagher, D.W. Johnson Jr., Thermochim. Acta. 14 (1976) 255.

[4] K.M. Caldwell, P.K. Gallagher, D.W. Johnson Jr., Thermochim. Acta. 18 (1977) 15.

[5] D.T. Livey, J.S. O'Neill, A.W. Hey, in: R.M. Fulrath (Ed.), Proceedings of the 3rd International Material Symposium, 1966, Wiley, New York, 1968, pp. 800–827.

[6] J. Opfermann, J. Therm. Anal. Cal. 60 (2000) 641.

[7] H.J. Flammersheim, N. Eckardt, W. Kunze, Thermochim. Acta. 187 (1991) 269.

[8] ASTM E 698 (1979 rev. 1993), Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials, American Association for Testing Materials, Philadelphia, PA.

[9] J.P. Kyobe, A.M. Mulokozi, MS thesis, University of Dar es Salaam, Tanzania, submitted for publication.

[10] A.K. Galwey, M.E. Brown, Thermal Decomposition of Ionic Solids, Elsevier, Amsterdam, 1999 (Chapter 5.5).

[11] M. Arnold, G.E. Veress, J. Paulik, F. Paulik, in: H.G. Wiedemann (Ed.), Proceedings of the ICTA, 1980, Birkhaeuser Verlag, Basel, 1980, p. 69.

[12] P.K. Gallagher, D.W. Johnson Jr., Thermochim. Acta. 14 (1976) 255.

[13] G.C. McBane, J. Chem. Ed. 75 (1998) 919.