Thermochimica Acta, 51 (1981) 225—231
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

THE CONVERSION OF KINETIC DATA TAKEN AT CONSTANT TIME INCREMENTS TO CONSTANT REACTION INCREMENTS *

D.W. JOHNSON, Jr. and P.K. GALLAGHER

Bell Laboratories, Murray Hill, NJ 07974 (U.S.A.)

(Received 27 May 1981)

ABSTRACT

Modern methods of data acquisition for studying the kinetics of solid state reactions often result in data on the degree of completion of reaction at equally spaced time intervals. Unless the reaction rate is constant with time, this leads to kinetic results which are usually weighted in favor of the latter portions of the reaction. We illustrate methods for converting such data to avoid this effect, but show that for well-behaved systems such as the decomposition of $CaCO_3$, these precautions do not significantly affect the kinetic results. Conditions are outlined where these techniques should be used to avoid error.

INTRODUCTION

The determination of solid state reaction kinetics often relies on data taken at constant time intervals. For example, solid state decompositions studied isothermally frequently make use of TG (thermogravimetry) data taken by machine at preset intervals of time. Analysis of this data involves the calculation of the fraction reacted (α) at each of these times and then fitting these α vs. time points to any of the numerous expressions used to describe kinetics models.

Except for the rare case in which α is directly proportional to time, equal intervals of time between data points result in unequal intervals of α between the same data points. Because decomposition reactions nearly always show a monotonic decrease in $d\alpha/dt$ with time, data taken at equal time intervals result in a compression of the data points at the higher values of α. If then, in fitting the data to kinetic equations, all data points are weighted equally, the degree of fit to any particular kinetic equation is influenced more by the data at high values of α than it is at low values of α. In principle, to compare various kinetic equations, those equations which best fit the data at the higher values of α are favored over those which fit the data equally well at low values of α.

The purpose of this work is to develop methods for transforming data taken at equal time intervals to data points at equal α intervals and to compare the results of kinetic analyses of both data types.

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* Presented at the 11th Annual NATAS Meeting, New Orleans, LA, Oct. 15—18, 1981.

TECHNIQUE

Data on the thermal decomposition of $CaCO_3$ were used. These were taken from a study [1] of the effects of sample size on decomposition kinetics. The isothermal data were taken from a thermobalance and machine recorded at equal intervals of time. Ranges of temperatures and heating rates had been used and this offered data sets with both many and few data points and with both well-behaved and noisy signals.

In order to derive a set of data points equally spaced in α from a set of points equally spaced in time, some sort of interpolation is necessary. Furthermore, unless the data set is very well behaved, a degree of data smoothing may also be desirable or necessary since α vs. t must be monotonically increasing in order to avoid multiple values of α at a single value of t *.

In the course of this work, we have tried two interpolation and smoothing techniques. These are the fitting of *B* splines and the fitting of polynomials.

B splines [2] are piecewise polynomials fit over sections of data such that the function and certain derivatives of the function are continuous at the nodes (the intersections of the data sections). This technique has the advantage that it can be used on data sets whose behavior is not well approximated by polynomials and is well suited to computation by machine. We have found that *B* splines also can have the disadvantage that, under some conditions of noisy data, they follow the data points sufficiently well that multiple roots in the α vs. t function can occur. An example of this is shown in Fig. 1. These data were taken on the smallest sample used, 1 mg. Consequently, the considerable noise in the data signal from the thermobalance gives a set of data which without sufficient smoothing gives a function with multiple values of time for some values of α. In this case, a spline of order 6 was used with three data points per mesh interval.

Using more points per mesh interval for the data in Fig. 1 will lead to sufficient smoothing to avoid negative first derivatives in the function. In the extreme, an extension of this leads to a single mesh interval with nodes only at the minimum and maximum values of time in the data set. This is equivalent to a polynomial fit which for the data sets in this study offered well-smoothed functions which also approximated the data points well. Figure 2 shows the same data as in Fig. 1 but with a cubic polynomial fit. For the data sets used in this study, we found the cubic polynomial fit to be satisfactory and subsequent data analyses will make use of it. However, the reader is cautioned that, for more complex reactions than the decomposition of $CaCO_3$, it would be desirable to use a spline or polynomial with more degrees of freedom. Also, while a cubic polynomial can fit perfectly data of a polynomial form such as reaction order 0 or $\frac{1}{2}$, it can never exactly fit other reaction equations such as some derived from the diffusion controlled models.

From the polynomial used to smooth the α vs. t data, the times corre-

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* The nature of data acquisition in thermal analysis can readily lead to multiple roots in $\alpha = f(t)$ due to noise in the measuring signal for α. On the other hand, there are seldom multiple roots in the $t = f(\alpha)$ function since the recorded values of time are monotonically increasing.

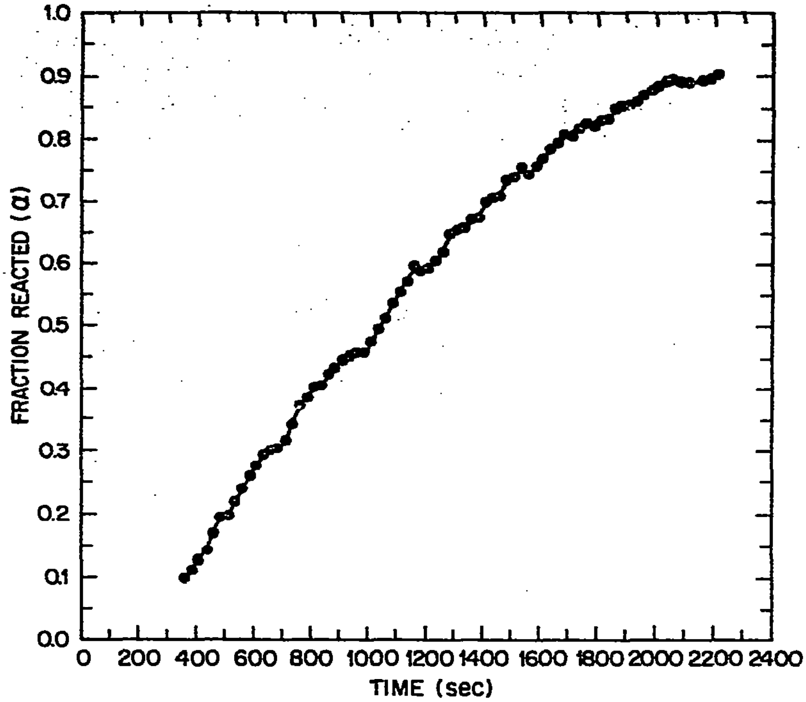

Fig. 1. Spline fit to data points for 1 mg $CaCO_3$ decomposed at 930 K. The spline order is 6 with 3 points per mesh interval.

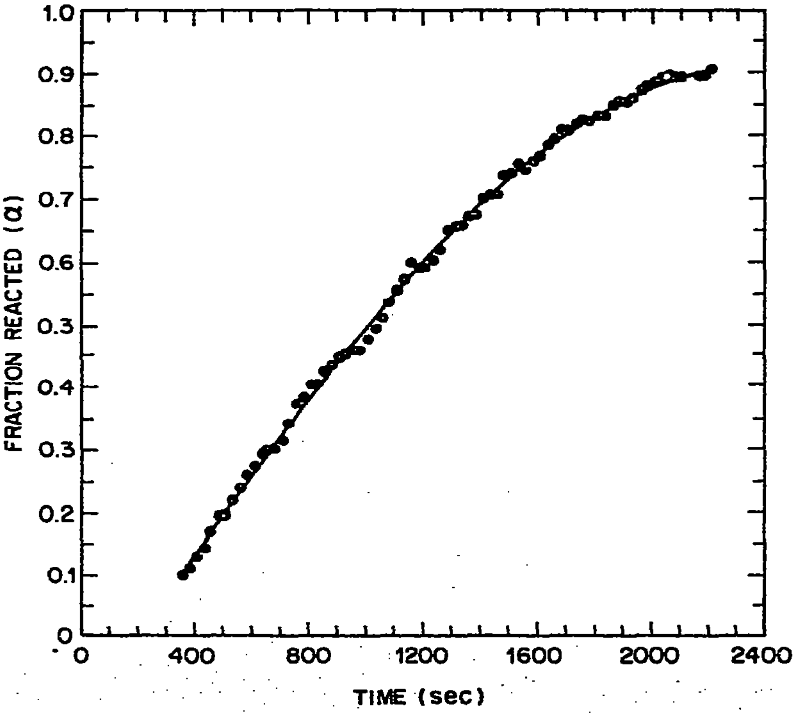

Fig. 2. A cubic polynomial fit to the same data set as Fig. 1.

sponding to 0.01 increments of α were calculated and these α vs. t data sets as well as the original α vs. t sets were used to determine the best kinetic equation over the range $0.1 \leqslant \alpha \leqslant 0.9$. The kinetic models used and the computational methods have been described elsewhere [3].

RESULTS

As reported in the previous study, the contracting area model $[1 - (1 - \alpha)^{1/2} = kt]$ and the Erofeev, $n = 2$ model $[-\ln(1 - \alpha)^{1/2} = kt]$ fit the data spaced equally in time quite well. Examples of the data and the least squares straight lines for the Erofeev, $n = 2$, equation are shown in Figs. 3 and 4. Shown in these figures are both the original data points equally spaced in time (left axis) and the calculated points equally spaced in α (right axis). Note that the left and right vertical axes are displaced to avoid overlap of data points. Figure 3 represents a case where the original data points were well behaved in that only a small amount of noise existed. In Fig. 4, considerably more noise was present in the original data. However, in both cases virtually the same straight line was calculated for both the data equally spaced in time and those equally spaced in alpha. The data smoothing in Fig.

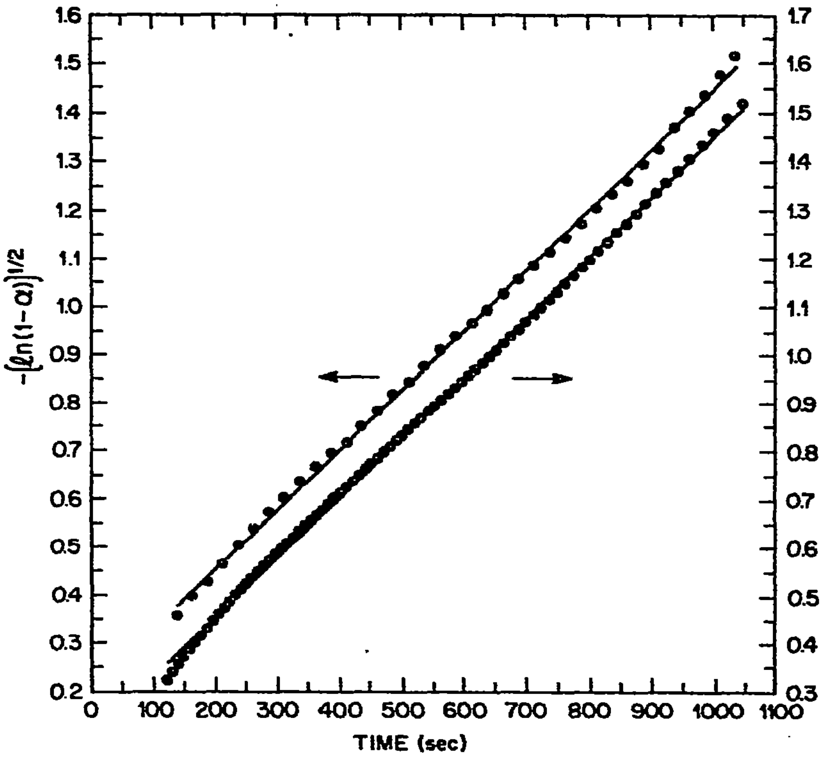

Fig. 3. 2 mg samples of $CaCO_3$ decomposed at 952 K and plotted according to the Erofeev, $n = 2$, model. The lines are the least squares straight lines fitting either conventional data equally spaced in time (left axis) or derived data equally spaced in α (right axis). Note that the two vertical axes have been displaced to avoid overlap of the data.

TABLE 1

Rate constants for the Erofeev, $n = 2$, model

Sample weight (mg)		Rate constant (sec^{-1})				
		880 K	910 K	930 K	952 K	981 K
1	Equal time	1.90×10^{-4}	5.68×10^{-1}	6.47×10^{-4}	1.42×10^{-3}	3.02×10^{-3}
	Equal α	1.90×10^{-4}	5.66×10^{-4}	6.60×10^{-4}	1.42×10^{-3}	3.00×10^{-3}
2	Equal time	1.38×10^{-4}	3.83×10^{-4}	6.51×10^{-4}	1.24×10^{-3}	2.13×10^{-3}
	Equal α	1.40×10^{-4}	3.83×10^{-4}	6.46×10^{-4}	1.24×10^{-3}	2.13×10^{-3}
4	Equal time	1.04×10^{-4}	1.74×10^{-4}	3.71×10^{-4}	6.77×10^{-4}	1.49×10^{-3}
	Equal α	1.03×10^{-4}	1.74×10^{-4}	3.70×10^{-4}	6.78×10^{-4}	1.49×10^{-3}
8	Equal time	6.16×10^{-5}	1.28×10^{-4}	2.86×10^{-4}	4.64×10^{-4}	1.02×10^{-3}
	Equal α	6.14×10^{-5}	1.28×10^{-4}	2.86×10^{-4}	4.65×10^{-4}	1.01×10^{-3}
16	Equal time	3.98×10^{-5}	8.39×10^{-5}	1.87×10^{-4}	3.31×10^{-4}	6.13×10^{-4}
	Equal α	4.00×10^{-5}	8.38×10^{-5}	1.88×10^{-4}	3.31×10^{-4}	6.15×10^{-4}
32	Equal time	3.31×10^{-5}	5.42×10^{-5}	1.04×10^{-4}	1.96×10^{-4}	4.09×10^{-4}
	Equal α	3.32×10^{-5}	5.43×10^{-5}	1.05×10^{-4}	1.97×10^{-4}	4.12×10^{-4}

TABLE 2

Activation energies and pre-exponential terms for the Erofeev, $n = 2$, model

		Sample wt. (mg)					
		1	2	4	8	16	32
Activation energy (kcal $mole^{-1}$)	Equal time	46.3	50.3	49.1	46.3	47.0	43.7
	Equal α	46.5	50.0	49.1	46.3	47.0	43.8
Pre-exponential term	Equal time	6.67×10^{7}	3.96×10^{8}	1.33×10^{8}	1.79×10^{7}	1.76×10^{7}	1.96×10^{6}
	Equal α	7.42×10^{7}	3.27×10^{8}	1.38×10^{8}	1.77×10^{7}	1.74×10^{7}	2.03×10^{6}

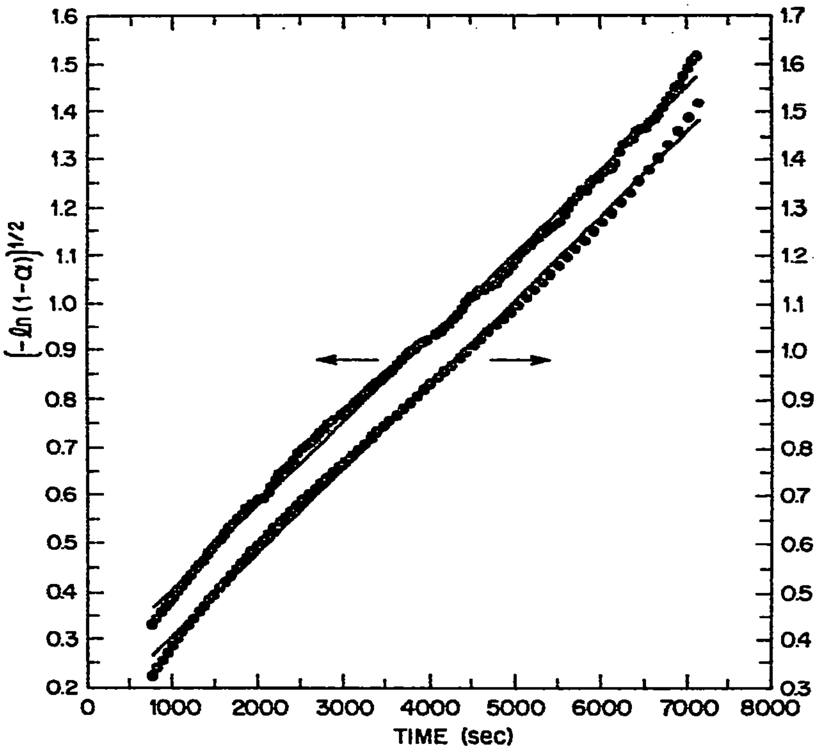

Fig. 4. As Fig. 3 but for a 4 mg sample of $CaCO_3$ decomposed at 910 K.

4 for the points equally spaced in α had a negligible effect on the nature of the fitting of this model.

The insensitivity to the type of data used is further illustrated in Table 1. Here the rate constants for all of the isothermal data sets are listed for both the original data points equally spaced in time and the calculated points equally spaced in α. The rate constants changed by, at most, 2% between the two data representations.

Table 2 further shows that the activation energies and pre-exponential terms are little affected by the type of data.

DISCUSSION AND CONCLUSIONS

While, in principle, the compression of data points taken at equal time intervals toward high values of α, can affect the derived kinetic results, no such effect has been found for a large body of data on the isothermal decomposition of $CaCO_3$. We found no significant changes in the kinetic model which best described the data, or the kinetic parameters derived from it despite the use of a rather crude smoothing function (cubic polynomial) to derive data spaced equally in α.

This suggests that the data fits the model equally well over the entire range of α used. In other words, if the data had fit one model best at low values of

α and another model at high values of α, then the use of data points equally spaced in t would have favored the model fitting best at high values of α.

Our results suggest to us that there is no need to smooth raw α vs. t data routinely and calculate equally spaced α data sets for studies of well-behaved systems such as $CaCO_3$. There are, however, two cases where the kinetic analyst should consider the techniques described here. One is for systems in which the model used to derive the kinetic information obviously fits better on one section of the reaction than others. The other is where the data are taken and analyzed over a very large range of α, probably to $\alpha > 0.95$, where a large fraction of data points equally spaced in time are clustered at the high values of α.

ACKNOWLEDGEMENT

The authors wish to thank N.L. Schryer for major contributions and suggestions regarding the curve fitting and smoothing techniques used.

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