ELSEVIER

Thermochimica Acta 290 (1996) 73–83

thermochimica acta

The use of the Harcourt and Esson relationship in interpreting the kinetics of rising temperature solid state decompositions and its application to pharmaceutical formulations

David Dollimore *, Supaporn Lerdkanchanaporn, Kenneth S. Alexander

Department of Chemistry and College of Pharmacy, The University of Toledo, Toledo, OH 43606-3390, USA

Received 12 February 1996; accepted 10 July 1996

Abstract

A new approach to establishing kinetic parameters for solid state decompositions is outlined based on the equation of Harcourt and Esson. It enables the integral method to be used without the need to make approximations. It is applied here to a study of certain pharmaceutical excipients used in the formulation of tablets.

Keywords: Kinetics; Solid state decompositions

1. Introduction

The Arrhenius equation is used in almost all kinetic analysis in spite of the fact that a considerable number of results quoted in the literature show deviant behavior. Frost and Pearson [1] list a series of deviant behavior patterns but the most common deviant behavior is several linear regions in the plot of log k (rate constant) against reciprocal temperature, or even a continuous curve which can be regarded as an infinite collection of linear regions. This kind of abnormal behavior is especially common in solid state decompositions. The relationship expressed as:

$$\log k = \frac{A'}{T} + \text{constant} \qquad (1)$$

where k is the specific reaction rate, was first put forward by Hood [2]. The subject has been reviewed by Laidler [3]. Here A' is a constant and T the temperature in degrees Kelvin. This type of expression was opposed by Harcourt and Esson [4] who claimed that the relationship was:

$$k = \text{constant} \times T^m \qquad (2)$$

where m is positive. Laidler points out that the parameters in the Harcourt and Esson equation have been given no physical significance. Recognizing the validity of the van't Hoff relationship [5] caused Arrhenius [6] to recast the experimental relationship of Hood into the form we now recognize as the Arrhenius equation:

$$\ln k = \ln A + -\frac{E}{RT} \qquad (3)$$

or

$$k = Ae^{-E/RT} \qquad (4)$$

---

* Corresponding author.

PII: S0040-6031(96)03063-8

where A is the pre-exponential factor and $\exp(-E/RT)$ is proportional to the number of molecules possessing energy in excess of E at the temperature T, commonly termed the energy of activation.

In this connection, plots of $\ln k$ against $1/T$, and $\ln k$ against T usually appear to be reasonably linear over the narrow temperature ranges used in kinetic studies because $1/T$, $\ln T$ and T are more or less linearly related themselves. Nevertheless in applying the Arrhenius equation to both homogeneous and heterogeneous processes, there are many recorded instances of extra terms being incorporated into the Arrhenius equation to accurately describe the experimental data [7–9].

However, an additional reason for a non-linear Arrhenius plot in solid state decomposition data, especially from rising temperature data, is the incorrect choice of the reaction mechanism equation leading to erroneous rate constant. It should be noted that the review by Laidler is confined to the isothermal determination of the reaction rate constant at each temperature and refers to homogeneous kinetic studies. For a review of the additional problems arising from rising temperature determinations of kinetic data, the paper by Flynn should be consulted [10].

In making application of the Arrhenius equation to the solid state reactions, one is restricted by the absence of a concentration term and the consequence of the kinetic laws based on geometric factors controlling the process at a reaction interface [11]. This leads to a nomenclature where one deals with the fraction decomposed (α) when the specific reaction rate (k) is defined as:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{5}$$

where t is the time, and $f(\alpha)$ is some function of α [12]. The occurrence in solid state decompositions of kinetic data showing two or more linear regions [12] or a curve [13] in the Arrhenius plots demonstrates an absolute need to test the dependence of the specific reaction rate (k) upon the temperature (T). This is often ignored in rising temperature methods which are often based implicitly on there being only a single set of Arrhenius parameters.

2. Theory

The usual approach for non-isothermal kinetic studies relating to solid state decompositions uses a linear rate of temperature increase from an initial value, T_0. Three equations are involved:

$$T = T_0 + \beta t \tag{6}$$

where β is the rate of temperature increase (dT/dt). The other two equations are the Arrhenius equation (Eq. 4) and the specific reaction rate expression (Eq. 5). This leads to:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\cdot\frac{dt}{dT} = \frac{kf(\alpha)}{\beta} \tag{7}$$

or

$$k = \frac{(d\alpha/dT)\beta}{f(\alpha)} \tag{8}$$

It should be noted that at this stage the calculation does not involve the Arrhenius equation. If the Arrhenius equation is assumed to be obeyed then:

$$\ln\left[\frac{(d\alpha/dT)\beta}{f(\alpha)}\right] = \ln A - \frac{E}{RT} \tag{9}$$

This approach is termed the differential method. The integral approach uses the relationship:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_i}^{T} e^{(-E/RT)}\,dT \tag{10}$$

where T_i is the initial temperature of the reaction and T is the temperature at some value of reaction decomposed (α) obtained by use of Eq. 7 and the Arrhenius equation (Eq. 4), and integrating. Unfortunately, the integral $\int e^{-E/RT}\,dT$ is incapable of an analytical solution, therefore alternative approximation methods have been used to evaluate this function [14–16]. Laidler did not deal with this problem. One method of overcoming this problem is to use the approach advocated by Flynn and Wall [17]. This results in a modelless evaluation of the energy of activation leaving the pre-exponential term and the reaction rate constant (and hence the reaction order) to be evaluated afterwards.

Another approach is to replace the Arrhenius equation with the Harcourt and Esson relationship

(Eq. 2) and again there are two methods of obtaining information from this approach, namely the differential method and an integral method.

In the differential method, the value of k is again given by Eq. 8 and the Harcourt and Esson relationship can be restated as:

$$k = C \times T^{m} \tag{11}$$

where C represents the constant in Eq. 2.
Then,

$$\log k = \log C + m \log T \tag{12}$$

or

$$\log \frac{(\mathrm{d}\alpha/\mathrm{d}T)\beta}{f(\alpha)} = \log C + m \log T \tag{13}$$

A plot of $\log[(\mathrm{d}\alpha/\mathrm{d}T)\beta/f(\alpha)]$ against $\log T$ then provides the value of m (from the slope) and C from the intercept. In the data provided in this article, the form of $f(\alpha)$ can be deduced by a selection procedure discussed later.

The Harcourt and Esson relationship (Eq. 11) can be used in an integral approach to a kinetic analysis which has the advantage over the integral approach of utilizing the Arrhenius equation. Using Eqs. 11, 8 we can write:

$$\frac{(\mathrm{d}\alpha/\mathrm{d}T)\beta}{f(\alpha)} = C T^{m} \tag{14}$$

hence

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{C}{\beta} \int_{T_i}^{T} T^{m}\,\mathrm{d}T \tag{15}$$

where T_i is initial temperature of reaction or transformation. This can be written as;

$$g(\alpha) = \frac{C}{\beta} \frac{T^{m+1}}{m+1} + \text{constant} \tag{16}$$

where

$$g(\alpha) = \int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)}$$

The general form of the relationship is thus:

$$g(\alpha) = B T^{m+1} + D \tag{17}$$

where B is equal to $C/[\beta(m+1)]$ and D is the "constant" term in Eq. 16. Thus if the reaction was first order, then it takes the form:

$$-\ln(1-\alpha) = B T^{m+1} + D \tag{18}$$

Thus if $g(\alpha)$ is plotted against T^{m+1} the plot should be linear, and B and D can be calculated.

If the Arrhenius parameters are required then we can take specific values of temperature in the temperature range where the reaction is noted. This point was noted by Laidler who set out the relationship between the various alternative forms of the Arrhenius expression (including the Harcourt and Esson relationship) and the Arrhenius activation energy. Then at temperature T_1:

$$k_{(T_1)} = C T_1^{m} = A e^{-E/RT_1} \tag{19}$$

and at temperature T_2:

$$k_{(T_2)} = C T_2^{m} = A e^{-E/RT_2} \tag{20}$$

when

$$\left[\frac{T_2}{T_1}\right]^{m} = \frac{e_2^{-E/RT_2}}{e_1^{-E/RT_1}} \tag{21}$$

or

$$m \ln\left[\frac{T_2}{T_1}\right] = \left[\frac{E}{R}\right]\left[\frac{\Delta T}{T_1 T_2}\right] \tag{22}$$

where ΔT is $T_2 - T_1$.

This will give the value for E and substituting back into Eq. 3 will give the value of A. However, the method can also be used to detect changes in E and note its dependence on α (see the earlier comments on the deviant behavior of the Arrhenius equation). The method is simply to take the value of ΔT as small increments of 2°C and scan the entire temperature range where the reaction or the transition is to be noted. The variation in E can then be plotted against the corresponding value of α taken as the mid-point of the ΔT increments in each case.

One point which needs further discussion is the number of kinetic mechanisms which describe solid state reactions. The models upon which these are based have been reviewed in detail by Brown et al. [11]. A computer program could cope with these reaction mechanisms by testing each of these in turn. This is a cumbersome approach and it is possible to narrow down the choice by considering the shape of the TG plot or other thermal analysis signal from which the α-T plot can be derived. This has been achieved in a simple manner by Dollimore and co-workers [18–23]. These workers showed that the choice of mechanism could be determined by a consideration of the following parameters:

i) α_{max} – this is the value of α at the maximum rate of decomposition for that step in the decomposition under consideration (as seen in the DTG plot).

ii) the half width defined as the width on the differential plot of $d\alpha/dT$ against T of the curve measured at the peak temperature with the base line between initial and final temperature (T_i and T_f experimentally).

iii) judging the character of the initial temperature (T_i) as diffuse ($T_{i(d)}$) or sharp ($T_{i(s)}$) and with similar designations for the final temperature T_f as $T_{f(d)}$ or $T_{f(s)}$

This will allow the separation of the various mechanisms into an individual mechanism or at the most two or three, thereby making the final testing of the kinetic mechanism much easier.

3. Experimental

3.1. Materials

The materials used were:

1. α-Cellulose (Lot # 100H0747) supplied by Sigma Inc.,
2. Microcrystalline cellulose (Avicel®, PH 101, Lot # 1401) supplied by FMC Corporation,
3. Stearic acid (Lot # 002680) supplied by Sherman Research Laboratories,
4. Silicon dioxide (Cab-O-Sil®, Grade M5, Lot # 1E252) supplied by Cabot Corporation.

3.2. Technique

A simultaneous TGA and DTA unit (TA SDT 2960) was used in the present study. The heating rate was 10°C min^{-1}, and the experiments were carried out in a flowing atmosphere of dry nitrogen (flow rate 50 mL/min). The sample and the reference cell were alumina. The sample mass was varied from 7 to 13 mg depending on the nature of materials. The reference cell was left empty.

4. Results and discussion

The TG data for α-cellulose are given in Fig. 1, for Avicel in Fig. 2, for stearic acid in Fig. 3. Silicon dioxide showed no alteration in mass up to 1000°C. Fig. 4 shows the TG signal for the binary mixture (1 : 1 by mas) of Avicel with silicon dioxide. From these the plots, fraction decomposed (α) against temperature (T) could be constructed and the α-T plot for Avicel is shown as an example in Fig. 5.

The set of α values is used to compute and construct the plot of $d\alpha/dT$ against temperature in Kelvin. These plots were examined using the parameters outlined above to deduce the kinetic expression for the compounds under investigation. The D3, F1, D2, and F1 mechanisms are chosen for α-cellulose, Avicel, stearic acid, and the binary mixture of Avicel with silicon dioxide, respectively. At this point, the new approach employing the Harcourt and Esson relationship can be tested.

From Eqns. 12 and 13, the plot of log k against log T is constructed, as shown in Fig. 6 for α-cellulose as an example. The linear relationship between log k and log T with significant values of correlation coefficients is reported in Table 1. Besides the differential form [$f(\alpha)$] in Eq. 13, the integral form [$g(\alpha)$] shown in Eq. 17 can be tested as well. Table 2 summarizes the data in such plots together with the appropriate correlation coefficients.

From Eq. 17 and Table 2, the value of D is seen to be either zero or negligible and can be ignored. A plot of log [$g(\alpha)$] against log T can be carried out and a new relationship can be written as:

$$\log[g(\alpha)] = \log B + (m+1)\log T \qquad (23)$$

The value of m and log B can be calculated from a slope and an intercept, respectively. A typical plot of log [$g(\alpha)$] against log T is shown in Fig. 7.

Comparing the values of m for each compound obtained from Table 1 using Eq. 12 and from Table 3 which shows the data derived from Eq. 23, it is found that the m values for an individual compound from both equations (Eqs. 12 and 23) are quite close, especially for stearic acid.

Employing the Arrhenius parameters, and calculating the activation energy (E) in kJ mol^{-1}, using Eq. 22, the plot of E against α can be constructed, as shown in Figs. 8–11 for α-Cellulose, Avicel,

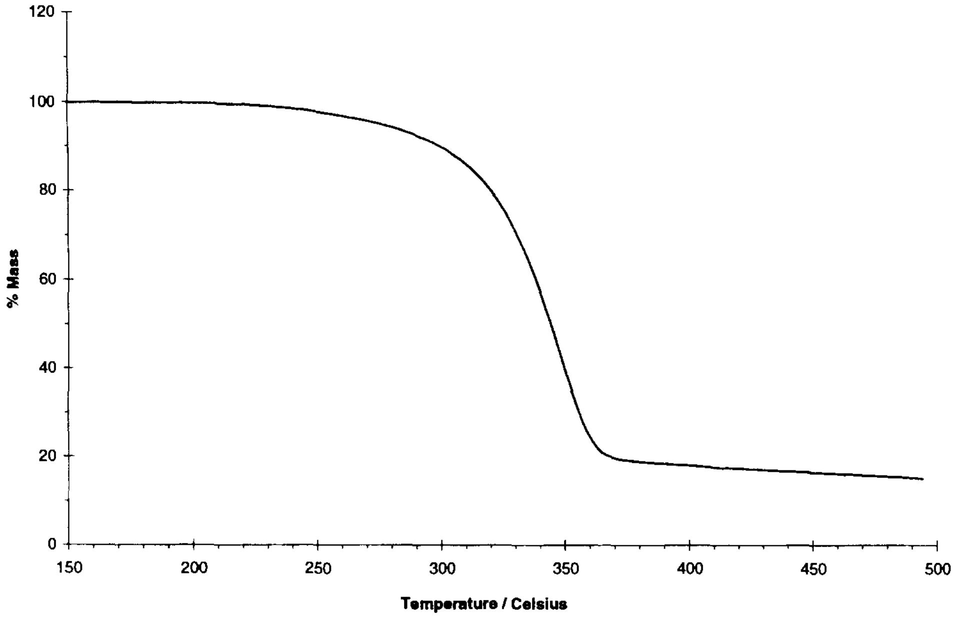

Fig. 1. TG plot for α-cellulose under an atmosphere of dry nitrogen.

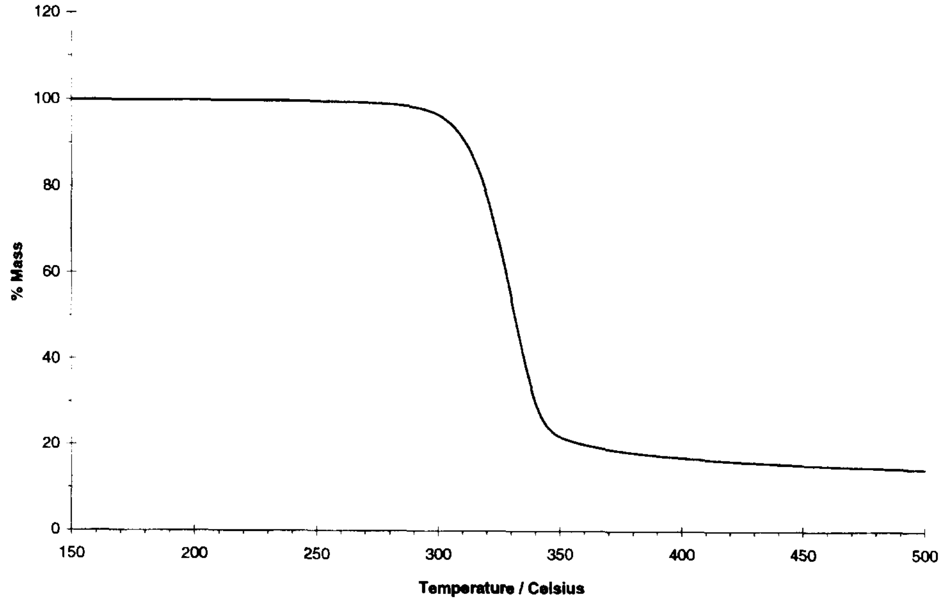

Fig. 2. TG plot for Avicel PH 101 under an atmosphere of dry nitrogen.

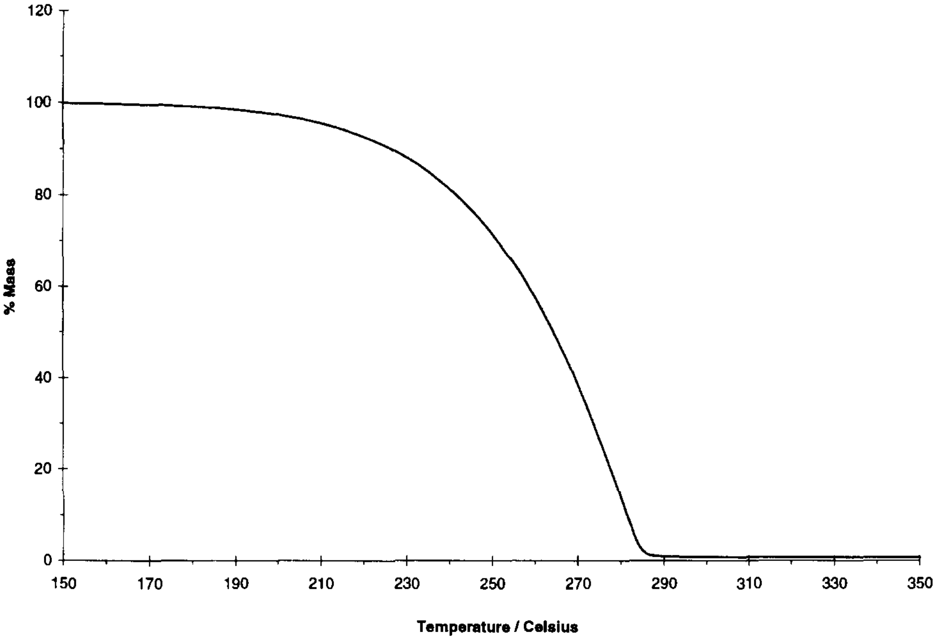

Fig. 3. TG plot for stearic acid under an atmosphere of dry nitrogen.

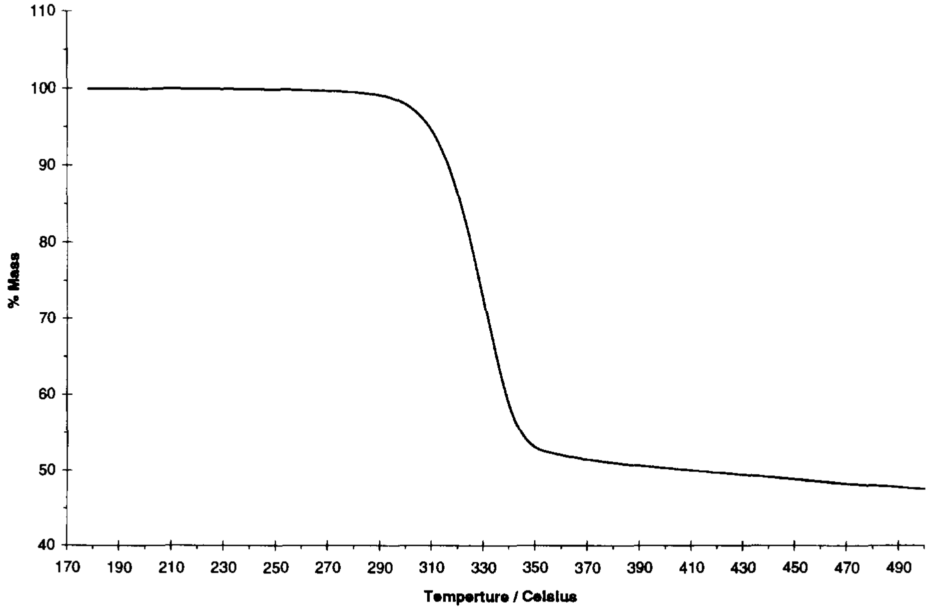

Fig. 4. TG plot for the binary mixture of Avicel PH 101 with silicon dioxide under an atmosphere of dry nitrogen.

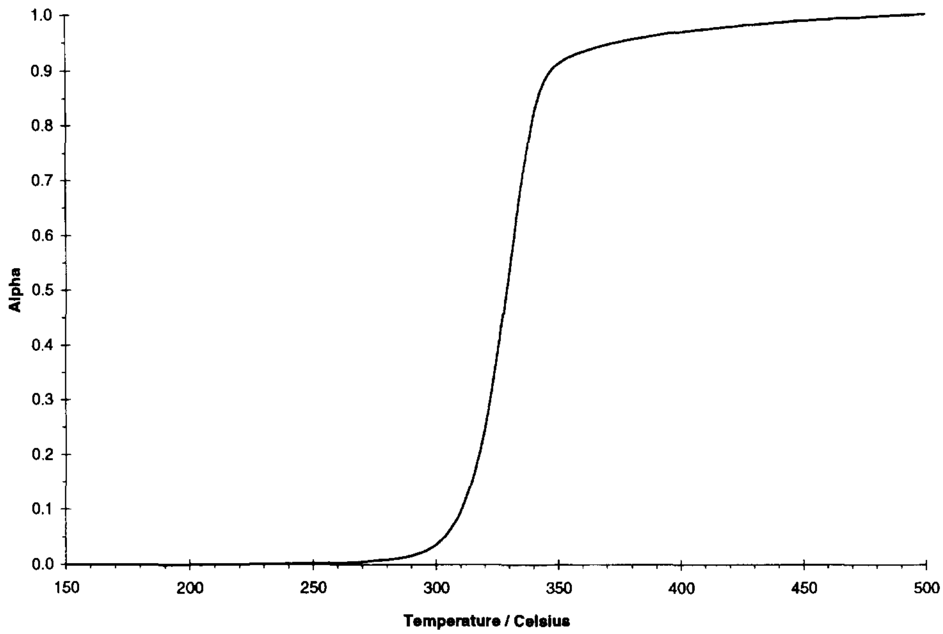

Fig. 5. α-T plot of Avicel PH 101 under an atmosphere of dry nitrogen.

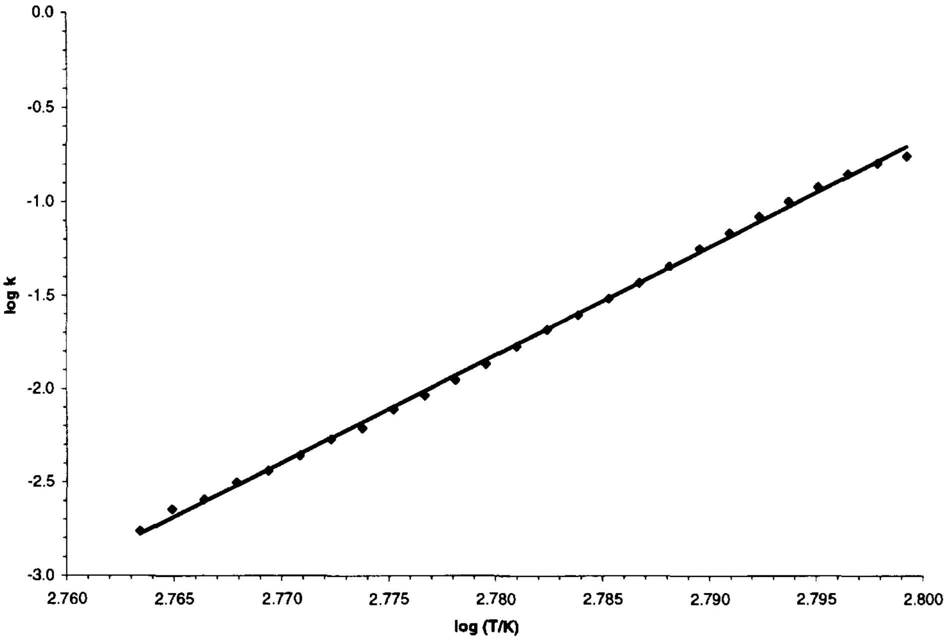

Fig. 6. Plot of log k against log (T/K) for α-cellulose degraded in nitrogen from $T = 580$ to 630 K, using the D3 mechanism.

Table 1
Data for plots of log k vs. log T (according to Eq. 12) together with correlation coefficient, R^2

Material (Kinetic mechanism)	log C	m(= slope)	R^2
α-Cellulose (D3)	−161.89	57.58	0.9988
Avicel PH 101 (F1)	−167.31	60.13	0.9978
Stearic acid (D2)	−127.41	46.35	0.9996
Avicel PH 101 + silicon dioxide (F1)	−149.58	53.73	0.9932

Table 2
Data for plots of $g(\alpha)$ against T^{m+1} (according to Eq. 17) together with correlation coefficient, R^2

Material (Kinetic mechanism)	B(= slope)	D	R^2
α-cellulose (D3)	2.27×10^{-165}	0.0	1.0000
Avicel PH 101 (F1)	8.40×10^{-171}	0.0	1.0000
Stearic acid (D2)	8.00×10^{-131}	4.0×10^{-5}	0.9998
Avicel PH 101 + silicon dioxide (F1)	5.00×10^{-153}	2.8×10^{-3}	0.9984

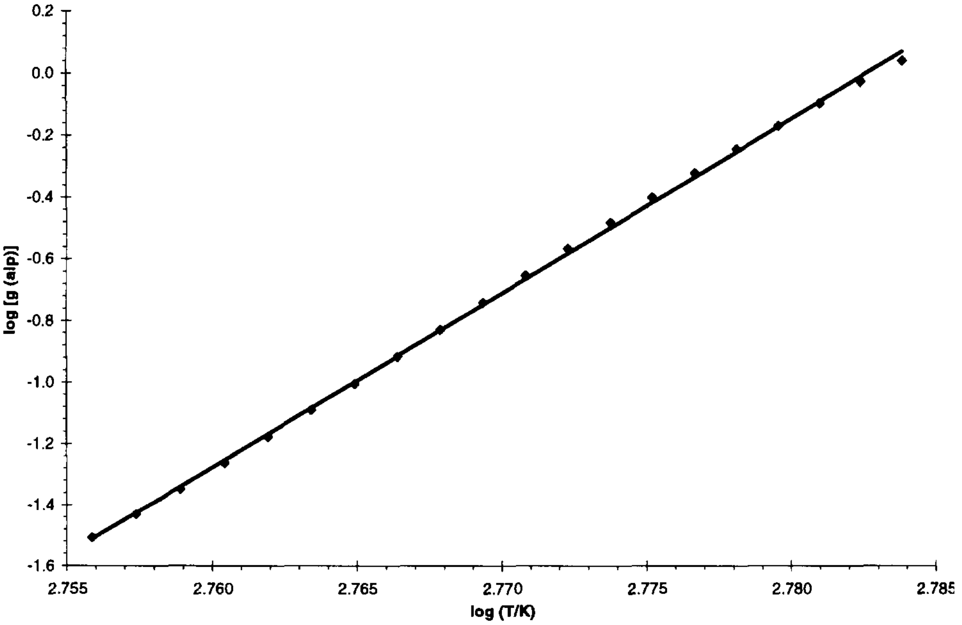

Fig. 7. Plot of log [$g(\alpha)$] against log (T/K) for the binary mixture of Avicel with silicon dioxide degraded in nitrogen from $T = 570$ to 608 K, using the F1 mechanism.

Table 3
Data for plots of log $[g(\alpha)]$ against log T (according to Eq. 23) together with correlation coefficient, R^2

Material	log B	$m+1$ (= slope)	R^2	m (from Eq. 23)	m (from Table 1, Eq. 12)
α-cellulose	−150.64	53.56	0.9963	52.56	57.58
Avcel PH 101	−157.69	56.66	0.9978	55.66	60.13
Stearic acid	−132.27	48.15	0.9993	47.15	46.35
Avicel PH 101 + silicon dioxide	−156.99	56.42	0.9994	55.42	53.73

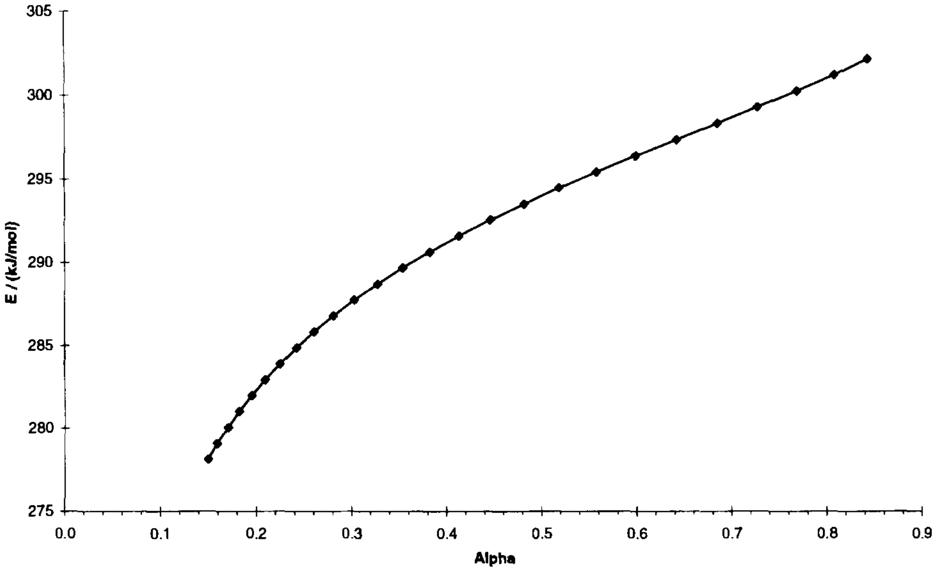

Fig. 8. Plot of E/(kJ mol^{-1}) against alpha for α-cellulose degraded in nitrogen from $T = 464$ to 556 K, using the D3 mechanism.

Stearic acid, and the binary mixture of Avicel with Silicon dioxide, respectively. These plots show the increasing E values when the values of α increase. If log E is plotted against α, it yields a linear relationship.

This approach based on the equation of Harcourt and Esson to establish the kinetic parameter for solid state decompositions is described. It enables the integral method to be employed without the need to make approximations.

The effect of silicon dioxide might be that of a diluent in that it would reduce the contact points between microcrystalline cellulose particles or aggregates, thereby reducing the spread of the reaction interface from one particle to another via the points of contact. However, the mechanism is F1 in both cases and the value of E at $\alpha = 0.5$ is only 302 kJ mol^{-1} for Avicel and 270 kJ mol^{-1} for the mixture. This suggests that spread of the degradation process via contact points between particles may not be significant.

It must be noted that this approach (and many like it) is dependent on the use of a constant form of $f(\alpha)$, and thereby $g(\alpha)$, throughout each reaction

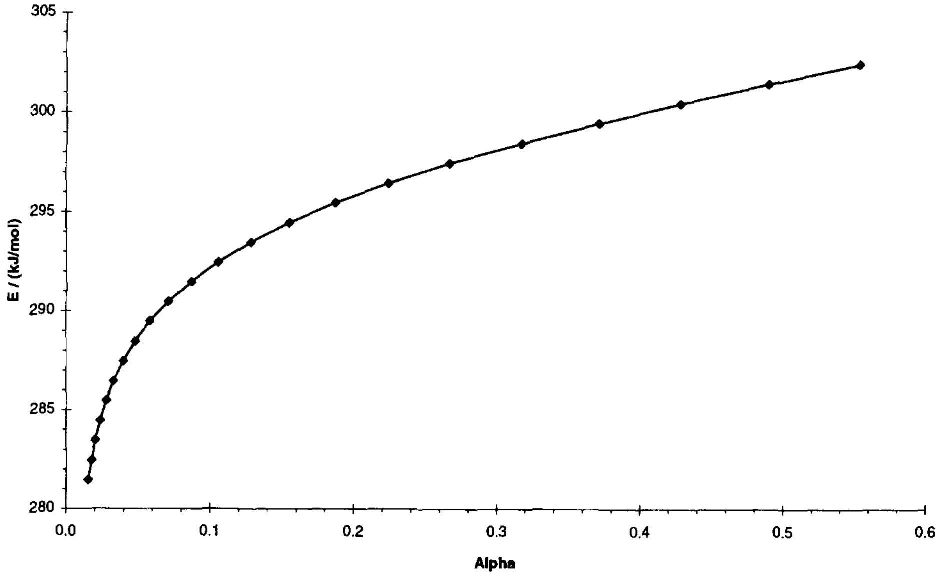

Fig. 9. Plot of E/(kJ/mol^{-1}) against Alpha for Avicel degraded in nitrogen from $T = 562$ to 604 K, using the F1 mechanism.

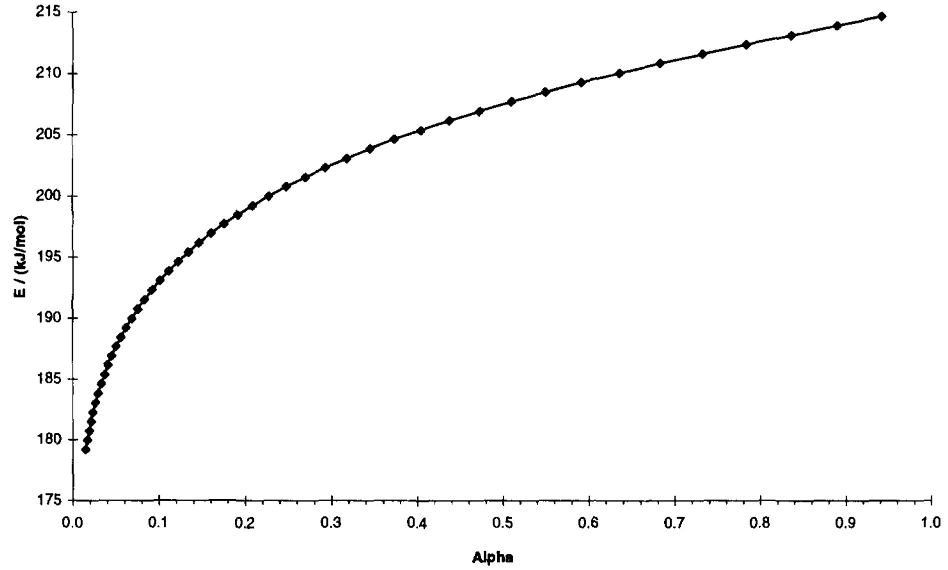

Fig. 10. Plot of E/(kJ mol^{-1}) against alpha for Stearic acid degraded in nitrogen from $T = 464$ to 556 K, using the D2 mechanism.

considered. It is, of course, possible that $k(\text{T})$ calculated by this assumption can show deviant Arrhenius behavior. However, the alternative is an alteration in $f(\alpha)$ occurring which would also show deviant Arrhenius behavior. A further alternative is that changes occur in both $f(\alpha)$ and $k(\text{T})$. This problem will be discussed in some detail in further publications.

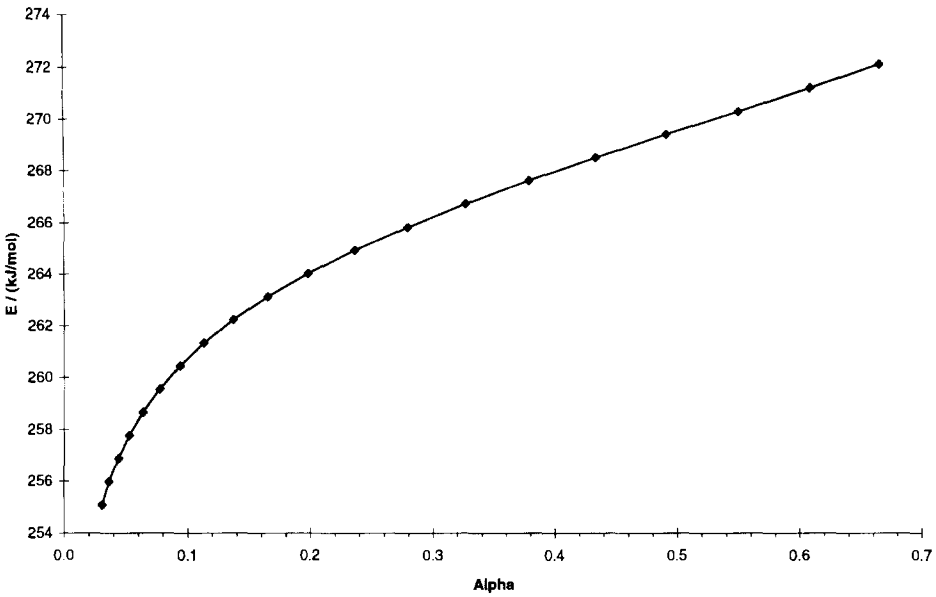

Fig. 11. Plot of E/(kJ mol^{-1}) against alpha for the binary mixture of Avicel with silicon dioxide degraded in nitrogen from $T = 570$ to 608 K, using the F1 mechanism.

A further point to note is that log [$g(\alpha)$] versus log T plots have in fact been used before but the approach here is different. It follows when assuming a first order reaction where $g(\alpha) = \log(\alpha)$. For example, Vallet [24] makes this approach. Approaches of this kind are given in Flynn's article [10] and the present authors are grateful for discussions with that author on the present subject.

References

[1] A.A. Frost and R.G. Pearson, Kinetics and Mechanism, Wiley, New York, (1993) 23.
[2] J.J. Hood, Phil. Mag., 6 (1878) 731; 20 (1885) 323.
[3] K.J. Laidler, J. of Chem. Educ., 61 (1984) 494.
[4] A.V. Harcourt and W. Esson, Phil. Trans. R. Soc., London, Ser. A., 186 (1895) 187; 212 (1913) 187.
[5] J.H. van't Hoff, Etudes de Dynamique Chemique, Muller, Amsterdam, (1884).
[6] S. Arrhenius, Z. Physik. Chem., 4 (1889) 226.
[7] D.M. Kooij, Z. Phys. Chem., 12 (1893) 155.
[8] M. Trautz, Z. Phys. Chem., 66 (1909) 496.
[9] J. Spohr, Z. Phys. Chem., 2 (1888) 194.
[10] J.H. Flynn, in R.F. Schwenker and P.D. Garn (Eds.), Thermal Analysis (2nd ICTA) Vol. 2, Academic Press, New York, (1969), pp. 1111–1126.
[11] M.E. Brown, D. Dollimore and A.K. Galwey, in C.H. Bamford and C.F.H. Tipper (Eds.), Comprehensive Chemical Kinetics, Vol. 22, Reactions in the Solid State, Elsevier, Amsterdam, (1980), 340 pp.
[12] D. Dollimore, G.R. Heal and R.W. Krupay, Thermochim. Acta, 24 (1978) 293.
[13] D. Dollimore and P.F. Rodgers, Thermochim. Acta, 30 (1979) 273.
[14] V. Satava and F. Skvara, J. Am. Ceram. Soc., 52 (1969) 591.
[15] P.M. Madhusudanen, K. Krishnan and K.N. Ninan, Thermochim. Acta, 97 (1986) 189.
[16] C.D. Doyle, J. Appl. Polym. Sci., 6 (1962) 639.
[17] J.H. Flynn and L.A. Wall, J. Research NBS, 70A (1966) 487.
[18] D. Dollimore, T.A. Evans, Y.F. Lee and F.W. Wilburn, Thermochim. Acta, 188 (1991) 77; 198 (1992) 249.
[19] D. Dollimore, T.A. Evans, Y.F. Lee, G.P. Pee and F.W. Wilburn, Thermochim. Acta, 196 (1992) 255–265.
[20] D. Dollimore, J.Therm. Analysis, 38 (1992) 111.
[21] D. Dollimore, Thermochim. Acta, 203 (1992) 18.
[22] D. Chen, X. Gao and D. Dollimore, Anal. Instrum., 20 (1992) 137.
[23] X. Gao, D. Chen and D. Dollimore, Thermochim. Acta, 223 (1993) 75–82.
[24] P. Vallet, Comptes Rendus, Acad. Sci., 200 (1935) 315.