

## KINETIC PARAMETERS IN AVRAMI—EROFEEV TYPE REACTIONS FROM ISOTHERMAL AND NON-ISOTHERMAL EXPERIMENTS

T.J.W. DE BRUIJN, W.A. DE JONG and P.J. VAN DEN BERG

*Delft University of Technology, Julianalaan 136, 2628 BL Delft (The Netherlands)*

(Received 22 October 1980)

### ABSTRACT

The differential rate equations for some simple frequently occurring Avrami—Erofeev type transformations were solved for isothermal as well as non-isothermal reactions. It is shown that the expressions commonly used to extract kinetic parameters from non-isothermal experiments are obtained via an incorrect procedure. However, the correct kinetic parameters will result from application of these equations to certain types of transformation.

### INTRODUCTION

Non-isothermal reactions in solid systems involving formation and growth of nuclei are often analysed using equations which are also applied for the description of isothermal reactions. These equations are usually derived by differentiation of the integral expression for  $\alpha$ , a method valid for isothermal reactions only. The resulting expression for  $d\alpha/dt$  is then used to analyse non-isothermal reactions. Henderson [1] has questioned this procedure. Therefore, the fundamental equations for  $d\alpha/dt$  of some simple frequently occurring types of transformation are solved below for non-isothermal reactions and the resulting expressions compared to results of the above-mentioned procedure. To that end, the equations normally used to describe isothermal reactions are first given.

### ISOTHERMAL REACTIONS

The equations generally used for describing isothermal reactions in solid systems with nuclei formation and growth are

$$[-\ln(1 - \alpha)]^{1/n} = kt = g(\alpha) \quad (1)$$

and

$$-\ln(1 - \alpha) = k^* t^n = g^*(\alpha) \quad (2)$$

These equations are often called Avrami, Erofeev, Johnson/Mehl equations; a

TABLE 1

Summary of possible values for  $n$  for different mechanisms (after refs. 1 and 5)

Reaction mechanism	$n$	Reaction mechanism	$n$
Constant nucleation rate		Growth of a constant number of nuclei (rate of nucleation is zero)	
One dimensional growth	2	One-dimensional growth	1
Two-dimensional growth	3	Two-dimensional growth	2
Three-dimensional growth	4	Three-dimensional growth	3

combination of these names is also used. The value of  $n$  depends on the mechanism of the reaction, as follows from Table 1 where a summary is given of several values of  $n$  for different mechanisms based on constant or zero nucleation rate. If the nucleation rate changes,  $n$  is not constant: when the nucleation rate increases,  $n$  is higher than in the case of constant nucleation rate, and for a decreasing nucleation rate,  $n$  will lie between those for constant and zero nucleation rate.

The results obtained from eqns. (1) and (2) differ but can easily be converted into each other

$$g(\alpha) = g^*(\alpha)^{1/n} \quad (3)$$

hence

$$k^{*1/n} = k \quad (4)$$

$k^*$  and  $k$  are represented by the normal Arrhenius equation and hence

$$A^{*1/n} = A \quad \text{and} \quad E^*/n = E \quad (5)$$

To trace the origin of eqns. (1) and (2) some simple and specific reactions will be analysed in more detail.

For a reaction with a constant number of nuclei per unit length ( $N_1$ ), or when at the beginning of the reaction a constant number of nuclei is formed immediately (site saturation), and assuming one-dimensional growth, the reaction rate is given by

$$\frac{d\alpha}{dt} = N_1 k_1 dt \quad (6)$$

To take overlap of nuclei into account, the right-hand side of eqn. (6) must be multiplied by  $(1 - \alpha)$  [2,3]

$$\frac{d\alpha}{dt} = N_1 k_1 dt (1 - \alpha) \quad (7)$$

Integration results in

$$-\ln(1 - \alpha) = \int N_1 k_1 dt = \int k_g dt \quad (8)$$

For isothermal reactions  $k_g$  is constant, hence

$$-\ln(1 - \alpha) = k_g t \quad (9)$$

If nuclei grow isothermally in three dimensions with an equal rate constant for each dimension, and allowing for overlap

$$-\ln(1 - \alpha) = C_3 N_3 \left[ \int k_1 dt \right]^3 = k_g^3 t^3 \quad (10)$$

Equation (10) is generally written like eqn. [2]:  $-\ln(1 - \alpha) = k^* t^3$  or  $[-\ln(1 - \alpha)]^{1/3} = k_g t$  [eqn. (1)]. Equation (2) results is an overall value for all dimensions, eqn. (1) in a value for one dimension.

The rate expressions are different for reactions in which the number of growing nuclei increases. At constant nucleation rate the number of nuclei formed between  $t = \tau$  and  $t = \tau + d\tau$  is given by

$$dN = k_{f(n-1)} N_{f(n-1)} d\tau \quad (11)$$

If nuclei grow in one dimension, the change in length per unit length, or the conversion at time  $t$  for the nuclei formed between  $\tau$  and  $\tau + d\tau$  is:  $d\alpha_\tau = k_{f1} N_{f1} d\tau k_1 dt$  or  $d\alpha_\tau = k_f d\tau k_g dt$ ; on integration one finds

$$\alpha_\tau = k_f d\tau \int_\tau^t k_g dt \quad (12)$$

The total conversion is obtained by integration of eqn. (12) from  $\tau = 0$  to  $\tau = t$ . When allowing for overlap this results in

$$-\ln(1 - \alpha) = \int_0^t \left( k_f \int_\tau^t k_g dt \right) d\tau \quad (13)$$

For isothermal reactions

$$-\ln(1 - \alpha) = \frac{1}{2} k_f k_g t^2 \quad (14)$$

In the case of three-dimensional growth with  $k_1$  equal for all dimensions, we may write

$$d\alpha_\tau = k_{f3} N_{f3} d\tau C_3 [k_1 dt]^3 = k_f d\tau [k_g dt]^3 \quad (15)$$

which on integration for an isothermal reaction with overlap results in

$$-\ln(1 - \alpha) = \frac{1}{4} k_f k_g^3 t^4 \quad (16)$$

This can be written as  $-\ln(1 - \alpha) = k^* t^4$  [eqn. (2)] or  $[-\ln(1 - \alpha)]^{1/4} = k t$  [eqn. (1)]. Again, the normal substitutions of eqns. (4) and (5) may be used to convert values from eqn. (1) to eqn. (2) or vice versa. However, both equations [(1) and (2)] now result in overall values

$$k^* = \frac{1}{n} k_f k_g^{n-1} \quad \text{with } A^* = \frac{1}{n} A_f A_g^{n-1} \quad \text{and } E^* = E_f + (n - 1) E_g \quad (17)$$

and

$$k = \left[ \frac{1}{n} k_f k_g^{n-1} \right]^{1/n} \quad \text{with } A = \left[ \frac{1}{n} A_f A_g^{n-1} \right]^{1/n} \quad \text{and } E = \frac{E_f + (n - 1) E_g}{n} \quad (18)$$

$$A_f = N_{f(n-1)} A_{f(n-1)} \quad \text{and } A_g = C_{(n-1)}^{1/(n-1)} A_1 \quad (\text{for } n = 2, 3 \text{ and } 4) \quad (19)$$

The general equation relating conversion to time, taking into account overlap, is

$$\frac{d\alpha}{1-\alpha} = \int_0^t [G(t, \tau)]^m N_f(\tau) d\tau \quad (20)$$

in which  $G(t, \tau)$  is a measure for the size at time  $t$  of a nucleus formed at time  $\tau$  and equals normally:  $C_\tau^t \int k_1 dt N_f(\tau)$  gives the number of nuclei formed at time  $\tau$ . In isothermal reactions the  $G$  and  $N$  functions are usually constant and integration is straight forward, as was shown above.

Summarising, for growth of a constant number of nuclei, eqn. (1) results in activation energies for growth in one dimension, and use of eqn. (2) results in an activation energy  $n$  times the value obtained by using eqn. (1). For growth combined with nucleation overall values are obtained [see eqns. (17)–(19)].

### NON-ISOTHERMAL REACTIONS

Problems arise when non-isothermal experiments are performed which must be analysed. Some authors [4–7] use equations obtained by differentiating eqn. (1) and apply the equation obtained to describe the rate of non-isothermal reactions. However, the derivative of eqn. (1) is not valid for non-isothermal reactions and may be applied to describe isothermal transformations only, e.g. as applied by Erofeev [8]. Nevertheless, this incorrect procedure is often applied and will be shown here.

When eqns. (1) and (2) are differentiated the following equations result, respectively

$$\frac{d\alpha}{1-\alpha} = kn[-\ln(1-\alpha)]^{1-1/n} dt \quad (21)$$

$$\frac{d\alpha}{1-\alpha} = k^* nt^{n-1} dt \quad (22)$$

On integration

$$[-\ln(1-\alpha)]^{1/n} = g(\alpha) = \int k dt \quad (23)$$

and

$$-\ln(1-\alpha) = g^*(\alpha) = \int k^* nt^{n-1} dt \quad (24)$$

For isothermal reactions eqn. (3) is valid:  $g(\alpha) = [g^*(\alpha)]^{1/n}$ . However, for non-isothermal reactions this is generally not correct because  $k$  and  $k^*$  are not constant and

$$\int k dt \neq \left[ \int k^* nt^{n-1} dt \right]^{1/n} \quad (25)$$

If  $n = 1$  it is still correct of course. From this example it is seen that at least one of the derivatives of the equations valid for isothermal reactions may not

be applied to non-isothermal reactions. The correct procedure involves integration of the fundamental expression valid for  $d\alpha/dt$  such as eqn. (6). This integration is shown below, again for the simple cases previously described.

For a non-isothermal reaction with a constant number of nuclei, one-dimensional growth and taking into account overlap, eqn. (7) gives

$$\int \frac{d\alpha}{1-\alpha} = -\ln(1-\alpha) = \int \dot{N}_1 k_1 dt = \int k_g dt \quad (26)$$

For three-dimensional growth, with  $k_1$  equal for all dimensions, and with overlap

$$\int \frac{d\alpha}{1-\alpha} = -\ln(1-\alpha) = C_3 N_3 \left[ \int_0^t k_1 dt \right]^3 = \left[ \int_0^t k_g dt \right]^3 \quad (27)$$

or

$$[-\ln(1-\alpha)]^{1/3} = \int_0^t k_g dt \quad (28)$$

The general result is

$$[-\ln(1-\alpha)]^{1/n} = \int_0^t k_g dt \quad (29)$$

which is equal to eqn. (23). Thus, for a transformation with a constant number of nuclei (or site saturation), use of eqn. (23) results in correct values, although an incorrect procedure was followed for its derivation. This implies that use of eqn. (24) is not allowed [see eqn. (25)].

For a reaction with a constant nucleation rate the equation obtained for growth in  $n-1$  dimensions reads

$$\int \frac{d\alpha}{(1-\alpha)} = \int_0^t k_f \left[ \int_{\tau}^t k_g dt \right]^{n-1} d\tau \quad (30)$$

When instead of this relation eqn. (23) is applied, some overall values for the kinetic parameters will be obtained. However, at first sight it is not clear whether use of eqn. (23) with the substitutions valid for isothermal reactions [eqn. (18)] will result in the correct kinetic parameters, as in the case with reactions with a constant number of nuclei. To resolve this question, the integrals in eqns. (23) and (30) will be solved by approximation and the results compared.

First eqn. [23]:  $g(\alpha) = [-\ln(1-\alpha)]^{1/n} = \int k dt$ . Usually a linear heating rate is employed in non-isothermal experiments, thus  $T = T_0 + \beta t$  and  $dt = dT/\beta$ . With those substitutions eqn. (23) can be solved (cf. Doyle [9])

$$\begin{aligned} g(\alpha) &= \int_0^t k dt = \int_{T_0}^T A \exp \frac{-E}{RT} \frac{dT}{\beta} = -\frac{AE}{\beta R} \int_{x_0}^x \frac{\exp(-x)}{x^2} dx \\ &= -\frac{AE}{\beta R} \left[ \int_{x_0}^{\infty} \frac{\exp(-x)}{x^2} dx - \int_x^{\infty} \frac{\exp(-x)}{x^2} dx \right] \end{aligned} \quad (31)$$

with  $x = E/RT$ ;  $x_0$  being  $\gg x$ , the first integral can be neglected and eqn. (31) reduces to

$$g(\alpha) = \frac{AE}{\beta R} p(x) \quad (32)$$

with

$$p(x) = \int_x^\infty \frac{\exp(-x)}{x^2} dx \quad (33)$$

The function  $p(x)$  is approximated using the relation

$$\int_x^\infty e^{-x} x^{-b} dx \simeq x^{1-b} e^{-x} \sum_{m=0}^{\infty} \frac{(-1)^m (b)^m}{x^{m+1}} \quad (34)$$

as was done by Coats and Redfern [10]. When only the first term of this series is used the result is

$$g(\alpha) = [-\ln(1 - \alpha)]^{1/n} = \frac{AE}{\beta R} p(x) = \frac{AR}{\beta E} T^2 \exp\left(-\frac{E}{RT}\right) \quad (35)$$

Now eqn. (30) will be solved for  $n = 2$ , i.e. for nucleation and one-dimensional growth

$$-\ln(1 - \alpha) = \int_0^t k_f \left[ \int_\tau^t k_g dt \right] d\tau \quad (36)$$

First the integral on the right is solved, using the following substitutions

$$T = T_0 + \beta t, \quad dt = \frac{dT}{\beta}, \quad T_\tau = T_0 + \beta \tau, \quad d\tau = \frac{dT_\tau}{\beta}, \quad \frac{1}{T} = y \quad \text{and} \quad \frac{1}{T_\tau} = v$$

$$\begin{aligned} \int_\tau^t k_g dt &= \int_\tau^t A_g \exp\left(-\frac{E_g}{RT}\right) dt = -\frac{A_g}{\beta} \int_{1/T_\tau}^{1/T} \exp\left(-\frac{E_g}{RT}\right) T^2 d\left(\frac{1}{T}\right) \\ &= -\frac{A_g}{\beta} \int_v^y \frac{\exp\left(-\frac{E_g}{R} y\right)}{y^2} dy \\ &= \frac{A_g}{\beta} \left[ \int_y^\infty \frac{\exp\left(-\frac{E_g}{R} y\right)}{y^2} dy - \int_v^\infty \frac{\exp\left(-\frac{E_g}{R} y\right)}{y^2} dy \right] \\ &= \frac{A_g E_g}{\beta R} \left[ \int_x^\infty \frac{\exp(-x_g)}{x_g^2} dx_g - \int_{u_g}^\infty \frac{\exp(-x_g)}{x_g^2} dx_g \right] \end{aligned} \quad (37)$$

with

$$x_g = \frac{E_g}{R} y \quad \text{and} \quad u_g = \frac{E_g}{R} v \quad (38)$$

The integrals are again approximated by the first term of the function used by Coats and Redfern [eqn. (34)], resulting in

$$\int_{\tau}^t k_g dt = \frac{A_g E_g}{\beta R} \left[ \frac{\exp(-x_g)}{x_g^2} - \frac{\exp(-u_g)}{u_g^2} \right] \quad (39)$$

Substituted in (36)

$$-\ln(1 - \alpha) = \int_0^t k_f \times \frac{A_g R}{E_g \beta} \left[ T^2 \exp\left(-\frac{E_g}{RT}\right) - T_{\tau}^2 \exp\left(-\frac{E_g}{RT_{\tau}}\right) \right] d\tau \quad (40)$$

$$k_f = A_f \exp\left(-\frac{E_f}{RT_{\tau}}\right) \quad \text{and} \quad y_0 = \frac{1}{T_0} \quad \text{thus}$$

$$-\ln(1 - \alpha) = -\frac{A_f A_g R}{E_g \beta^2} \times \int_{y_0}^y \frac{\exp\left(-\frac{E_f}{R} v\right)}{v^2} \left[ \frac{\exp\left(-\frac{E_g}{R} y\right)}{y^2} - \frac{\exp\left(-\frac{E_g}{R} v\right)}{v^2} \right] dv \quad (41)$$

$$= -\frac{A_f A_g R}{E_g \beta^2} \left[ \frac{\exp\left(-\frac{E_g}{R} y\right)}{y^2} \times \int_{y_0}^y \frac{\exp\left(-\frac{E_f}{R} v\right)}{v^2} dv \right. \\ \left. - \int_{y_0}^y \frac{\exp\left(-\frac{(E_f + E_g)}{R} v\right)}{v^4} dv \right] \quad (42)$$

$v$  being the variable over which eqn. (42) is integrated. According to Doyle [9], the value of the integral for the lower limit is very small and can be neglected. Using the substitutions of eqn. (38) and the approximation of eqn. (34), the solution of eqn. (42) becomes

$$\frac{A_f A_g R}{E_g \beta^2} \left[ \frac{E_f}{R} \times \frac{\exp\left(-\frac{E_g}{R} y\right)}{y^2} \times \int_{x_f}^{\infty} \frac{\exp(-u_f)}{u_f^2} du_f - \frac{(E_f + E_g)^3}{R^3} \right. \\ \left. \times \int_{x_w}^{\infty} \frac{\exp(-u_w)}{u_w^4} du_w \right]$$

with

$$x_f = \frac{E_f}{R} y, \quad u_f = \frac{E_f}{R} v, \quad x_w = \frac{(E_f + E_g)}{R} y \quad \text{and} \quad u_w = \frac{(E_f + E_g)}{R} v$$

$$= \frac{A_f A_g R}{E_g \beta^2} \left[ \frac{R}{E_f} \times \frac{\exp\left(-\frac{E_g}{R} y\right)}{y^2} \times \frac{\exp\left(-\frac{E_f}{R} y\right)}{y^2} - \frac{R}{(E_g + E_f)} \right]$$

$$\times \frac{\exp\left\{-\frac{(E_f + E_g)}{R} y\right\}}{y^4} \Big] = \frac{A_f A_g R^2}{E_f E_g \beta^2} \times T^4 \times \exp\left\{-\frac{(E_f + E_g)}{RT}\right\} \left[1 - \frac{E_f}{(E_f + E_g)}\right] \quad (43)$$

For growth in two or three dimensions, eqn. (30) can be solved in the same manner, resulting in, respectively

$$-\ln(1 - \alpha) = \frac{A_f}{E_f} \left(\frac{A_g}{E_g}\right)^2 \left(\frac{R}{\beta}\right)^3 T^6 \exp\left\{-\frac{(E_f + 2E_g)}{RT}\right\} \left[1 - \frac{2E_f}{E_f + E_g} + \frac{E_f}{E_f + 2E_g}\right] \quad (44)$$

and

$$-\ln(1 - \alpha) = \frac{A_f}{E_f} \left(\frac{A_g}{E_g}\right)^3 \left(\frac{R}{\beta}\right)^4 T^8 \exp\left\{-\frac{(E_f + 3E_g)}{RT}\right\} \times \left[1 - \frac{3E_f}{E_f + E_g} + \frac{3E_f}{E_f + 2E_g} - \frac{E_f}{E_f + 3E_g}\right] \quad (45)$$

When eqn. (45) is raised to the power 1/4 it can be compared to eqn. (35) with  $n = 4$ . Into eqn. (35) we substitute for  $A$  and  $E$  the relations given in eqn. (18), valid for isothermal reactions. Thus, eqn. (35) becomes

$$g(\alpha) = [-\ln(1 - \alpha)]^{1/4} = \frac{(\frac{1}{4} A_f A_g^3)^{1/4} 4R}{(E_f + 3E_g) \beta} T^2 \exp\left\{-\frac{(E_f + 3E_g)}{4RT}\right\} \quad (46)$$

It is seen that this expression differs from eqn. (45) raised to the power 1/4, except when  $E_f = E_g$ .

To show the difference between eqns. (46) and (45) the conversion is calculated as a function of the temperature for some selected kinetic parameters. The result is shown in Fig. 1. Equation (46) results in slightly higher conversions than eqn. (45). The differences between the two equations

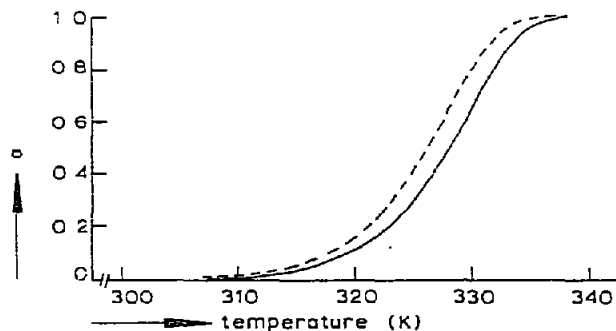


Fig. 1. Conversion as function of temperature calculated from eqns. (45) (—) and (46) (---), with  $A_f = 10^6 \text{ s}^{-1}$ ,  $E_f = 60 \text{ kJ mole}^{-1}$ ,  $A_g = 10^4 \text{ s}^{-1}$ ,  $E_g = 40 \text{ kJ mole}^{-1}$  and  $\beta = 0.03 \text{ K s}^{-1}$ .



depend mainly on the difference between  $E_f$  and  $E_g$ . Thus, the value for  $A$  obtained from eqn. (35) does not agree with those obtained from isothermal measurements. However, the temperature dependence of eqn. (46) is equal to that of eqn. (45); thus, the substitution  $E = [E_f + (n - 1)E_g]/n$  applies to the activation energy in (35) and equal values are found from isothermal and non-isothermal experiments. This means that eqn. (23) can also be applied to obtain the value of the activation energy of reactions with a constant nucleation rate.

Several authors [4,11,12] have stressed that, besides non-isothermal experiments, an isothermal experiment should always be performed when trying to establish the mechanism of a reaction. To find the mechanism as well as the activation energy from non-isothermal experiments,  $\ln g(\alpha)/T^2$  is usually plotted against  $1/T$ . When a straight line is found,  $g(\alpha)$  is considered to represent the correct mechanism. However, it can easily be shown that for all values of  $n$  straight lines will be obtained with activation energies depending on  $n$ . For example, assume a reaction involving nucleation and three-dimensional growth, i.e. that  $n = 4$ , eqn. (45) is then valid. The experimental results are analysed with eqn. (35) for  $n = 1, 2, 3$  and  $4$ . For  $n = 1$ ,  $\ln\{[-\ln(1 - \alpha)]/T^2\}$ , is in fact equal to  $\ln$ [eqn. (45)], which is

$$\ln\left[\frac{A_f}{E_f}\left(\frac{A_g}{E_g}\right)^3\left(\frac{R}{\beta}\right)^4 [1 - \dots]\right] + 6 \ln T - \frac{E_f + 3E_g}{RT}$$

A plot of  $\ln\{[-\ln(1 - \alpha)]/T^2\}$  against  $1/T$  will thus result in a straight line with an activation energy of about  $(E_f + 3E_g)$  because the change in the factor  $\ln T$  is negligible, the reaction usually occurring in a narrow temperature region. More generally speaking, the activation energy found for a given  $n$  value equals  $(E_f + 3E_g)/n$ . The activation energy thus depends on the value of  $n$ . This effect was indeed found experimentally by Dharwadkar et al. [11].

On the basis of the above, the use of the plot of  $\ln[g(\alpha)]/T^2$  against  $1/T$  is considered unsuitable for establishing the mechanism of a reaction. An isothermal experiment is necessary to find the correct value of  $n$  which in turn is needed to establish the activation energy. Only for the correct value of  $n$  are the activation energies from isothermal and non-isothermal experiments identical.

The above conclusion presupposes the use of eqn. (1). If eqn. (2) is used to derive the activation energy from isothermal experiments, one finds  $E = E_f + 3E_g$  and  $n = 4$ , whereas application of eqn. (23) [or (35)] for non-isothermal experiments results in  $E = (E_f + 3E_g)/n$ ; the activation energies derived from isothermal and non-isothermal experiments are no longer the same. Therefore, the use of eqn. (1) is preferred.

## CONCLUSIONS

The equations

$$[-\ln(1 - \alpha)]^{1/n} = kt \tag{1}$$

and

$$-\ln(1 - \alpha) = k^* t^n \quad (2)$$

may be used to describe the kinetics of isothermal reactions. Kinetic parameters from both equations can easily be converted into each other [eqn. (5)].

Although use of the derivative of eqns. (1) and (2) to analyse non-isothermal experiments is not correct, the use of the derivative of eqn. (1) results in the correct kinetic parameters for reactions with growth of a constant number of nuclei.

For reactions with nuclei growth and a constant rate of nucleation only overall values can be obtained. Here too, the derivative of eqn. (1) can be used to obtain the correct overall activation energy, but the overall pre-exponential factor  $A$  may differ from results obtained from isothermal experiments, depending on whether the activation energies for nucleation and growth differ much.

Analysis of a reaction with non-isothermal experiments only will not unequivocally reveal the correct mechanism, nor the correct activation energy. At least one isothermal experiment is necessary to establish the value of  $n$ . Only for the correct value of  $n$  will identical values for  $E$  result from isothermal and non-isothermal experiments; eqn. (1) and its derivative must then be used.

Since the derivative of eqn. (2) cannot be applied in interpreting non-isothermal experiments, the use of eqn. (1) or its derivative is recommended for analysing isothermal or non-isothermal experiments, respectively.

#### LIST OF SYMBOLS

$\alpha$	conversion
$A, A^*$	pre-exponential factors
$\beta$	heating rate ( $\text{K s}^{-1}$ )
$C, C_3, C_{n-1}$	form factors
$E, E^*$	activation energies ( $\text{kJ mole}^{-1}$ )
$G(t, \tau)$	growth function
$k, k^*$	reaction rate constants
$m$	number of dimensions in which growth occurs
$N$	number of nuclei (per unit length, surface or volume)
$N_{f1}, N_{f3}, N_{f(n-1)}$	number of potential growth nuclei ("germ nuclei") per unit ( $\text{length}$ ) $^{n-1}$
$N_f(\tau)$	number of nuclei formed at time $\tau$
$n$	order of reaction
$R$	gas constant ( $\text{kJ mole}^{-1} \text{K}^{-1}$ )
$T, T_0$	temperatures (K)
$t, \tau$	times
Subscripts	
$f$	For nuclei formation
$g$	For growth
1, 2, 3	Number of dimensions

## REFERENCES

- 1 D.W. Henderson, *J. Therm. Anal.*, 15 (1979) 325.
- 2 D.A. Young, *Decomposition of Solids*, The International Encyclopedia of Physical Chemistry and Chemical Physics, Vol. 1, Pergamon Press, Oxford, 1966.
- 3 Bel'kevich, *Vestn. Akad. Nauk Beloruss. S.S.R.*, 4 (1952) 120 from ref. 2.
- 4 J.M. Criado and J. Morales, *Thermochim. Acta*, 16 (1976) 382.
- 5 J. Sesták, *Proc. 3rd Int. Conf. Therm. Anal.*, Davos, Vol. 2, 1971, p. 3.
- 6 T. Palanisamy, J. Gopalakrishnan, B. Viswanathan, V. Srinivasan and M.V.C. Sastri, *Thermochim. Acta*, 2 (1971) 265.
- 7 F. Skvára and V. Satava, *J. Therm. Anal.*, 2 (1970) 325.
- 8 B.V. Erofeev, in J.H. De Boer (Ed.), *Reactivity of Solids*, Proc. 4th Int. Symp., Elsevier, Amsterdam, 1961.
- 9 C.D. Doyle, *J. Appl. Polym. Sci.*, 5 (15) (1961) 285.
- 10 A.W. Coats and J.P. Redfern, *Nature (London)*, 201 (1964) 68.
- 11 S.R. Dharwadkar, M.S. Chandrasekharaiah and M.D. Karkhanavala, *Thermochim. Acta*, 25 (1978) 272.
- 12 M.C. Ball and M.J. Casson, *Thermochim. Acta*, 2 (1978) 387.