

## THE EVALUATION OF KINETIC PARAMETERS FROM NON-ISOTHERMAL EXPERIMENTS: APPLICATION TO CRYSTALLIZATION KINETICS

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Kinetic parameters are usually evaluated from non-isothermal experiments by supposing the same form of the rate equation in isothermal and dynamic investigations. The capabilities and limitations of this approach will be discussed. The applicability of the alternative hypothesis where the transformed fraction is a state function of its variables and the rate equation is different under isothermal and non-isothermal conditions is highly questionable for any processes. This approach is definitely invalid for crystallization kinetics as it contradicts the formal theory of solid state transformations.

### 1. Introduction

A review paper has recently been published [1] on the non-isothermal investigation of crystallization kinetics. It is claimed that the usual practice of thermal analysis which works well with many different types of solid state transformations and chemical reactions is not applicable to this problem without significant modifications. The view is also expressed that the widely accepted relations are the result of a mathematically incorrect calculation of the time derivative of the transformed fraction equation. This derivative is calculated in ref. [1] and a dominant second term appears in the rate equation which is clearly absent in isothermal studies. In this way a modification is to be found when kinetics is investigated by non-isothermal methods.

This modification is treated in the literature [1–4] as something peculiar to crystallization kinetics. It does not seem to be recognized that discussions along the same lines have been going on since at least 1970 [5] as to whether a general correction exists for *any kind of processes* in non-isothermal investigations.

In this note we will first discuss the problem of crystallization kinetics. As the correct treatment has already been published [6–8] it is easily shown that the claims of ref. [1] are based on a misunderstanding. With the help of this example we will show the basic experimental observation of non-isothermal studies, viz. the transformed fraction is *not a state function* of its variables. It will also be emphasized that treatments based on an incorrect principle may

yield acceptable kinetic parameters. A thorough comparison of isothermal and dynamic studies of crystallization kinetics is however able to demonstrate the non-existence of the general correction term.

The basic equation of thermal analysis will also be discussed. It is intended to show that the problems discussed in refs. [1–3] in connection with the crystallization kinetics represent a special case of a general suggestion [5,9,10]. This alternative formulation of thermal analysis would predict a general correction term to the rate of any processes under non-isothermal conditions, while the transformed fraction is a state function of its variables. This view is generally found to be unacceptable for any processes [11–15] and it is also shown by some investigations [4,16] that there is definitely no justification for applying it to crystallization kinetics.

## 2. Crystallization kinetics

The treatment of ref. [1] is based on the formal theory of transformation kinetics [17–21]. The transformed fraction is

$$X = 1 - \exp\left(-g \int_0^t I_v \left(\int_{t'}^t u d\tau\right)^m dt'\right) \quad (1)$$

where  $g$  is a geometric factor,  $I_v$  and  $u$  are the (temperature dependent) nucleation and growth rates respectively. (Eq. (1) is strictly valid only for interface-limited growth, where  $m$  is equal to the number of growth dimensions,  $n$ . Diffusion-limited processes should in principle be treated by the diffusion equation, the solution of which can sometimes be approximated by the growth law:  $u \sim t^{1/2}$  [22].) Eq. (1) is integrated under isothermal conditions (when  $I_v$  and  $u$  are assumed to be independent of time) to yield

$$X = 1 - \exp(-kt^n) \quad (2)$$

which is redefined for the sake of convenience as

$$X = 1 - \exp[-(Kt)^n] \quad (3)$$

and  $K$  is assumed to have an Arrhenian temperature dependence

$$K = K_0 \exp(-E/RT). \quad (4)$$

The further treatment given in ref. [1] is based on two assumptions:

- (A) “Recent work by De Bruijn et al. [8] has shown that eq. (1) can be integrated under non-isothermal conditions ... to yield an expression having the form of eq. (3)”.
- (B) The usual practice of thermal analysis is based on a mathematically incorrect procedure: the time derivative of eq. (3) is calculated under non-isothermal conditions by neglecting the implicit time dependence of  $K[T(t)]$ .

The simplest case treated by De Bruijn et al. [8] will be discussed here as a

means of showing why the assumptions (A) and (B) of ref. [1] are not fulfilled. If a constant number of nuclei are growing isotropically in  $n$  dimensions then eq. (1) is reduced to eq. (29) of De Bruijn et al. [8]

$$[-\ln(1 - X)]^{1/n} = \int_0^t K [T(t')] dt' \neq K(T)t. \quad (5)$$

It is clear that eq. (5) does not yield eq. (3) under non-isothermal conditions (and has never been claimed to yield it in ref. [8]). The transformed fraction is obviously dependent on the  $T(t)$  path in eq. (5) while eq. (3) (which is valid in the isothermal case *only*) would yield the same transformed fraction for two different paths intersecting at point  $(t, T)$ .

The time derivative of eq. (5) yields the usual rate equation of thermal analysis for nucleation and growth limited processes

$$dX/dt = n(1 - X)[- \ln(1 - X)]^{(1-1/n)} K(T) \quad (6)$$

without any of the non-isothermal corrections suggested in ref. [1]. A real limitation of the conventional approach of thermal analysis (a quite different one from that suggested in ref. [1]) is also evident from refs. [6–8]: eq. (6) is used as a rate equation even in the more complicated cases (e.g. with non-zero nucleation rate) where it is not exactly valid.

Despite its limitations the usual approach based on eq. (6) as a rate equation is capable of reproducing an important experimental observation. If there are two different  $T-t$  paths (fig. 1) with the property  $T^{(1)}(t) > T^{(2)}(t)$  in the whole  $0 < t < t_1$  time interval, then  $X^{(1)}(t_1, T_1) > X^{(2)}(t_1, T_1)$ . This relation will be shown to be fulfilled in the Appendix for the special case of a linear  $T = T_0 + t(T_1 - T_0)/t_1$  and a hyperbolic  $T = T_0/[1 - t(1 - T_0/T_1)/t_1]$  temperature program. This behaviour is an undisputed experimental fact for the case of crystallization kinetics which behaviour is clearly not reproduced by eq. (3).

The misunderstanding in ref. [1] is undoubtedly caused by a number of previous publications where the procedure shown to be invalid by Yinnon and

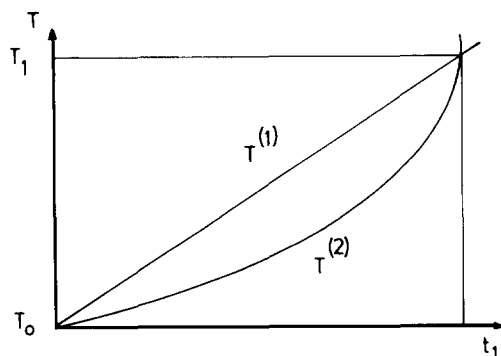


Fig. 1. Two time-temperature paths intersecting at  $(t_1, T_1)$ . Eq. (6) correctly predicts  $X^{(1)}(t_1, T_1) > X^{(2)}(t_1, T_1)$  for this case.

Uhlmann was in fact used. In these works [23–25] eq. (3) is used under non-isothermal conditions (an unjustified assumption) and in some cases its time derivative is calculated by neglecting the implicit time dependence of  $K[T(t)]$  (the second inconsistency). Following this procedure the correct eq. (6) was obtained, so the two unacceptable approximations perfectly cancel. Yinon and Uhlmann are right to point out that the correct time derivative of eq. (3) is

$$\frac{dX}{dt} = n(1-X)[- \ln(1-X)]^{(1-1/n)} K(T) \left( 1 + \frac{T-T_0}{T^2} \frac{E}{R} \right) \quad (6^*)$$

and it is not equal to eq. (6). One must however go one step further to recognize that eq. (3) should by no means be used under non-isothermal conditions.

The peculiarity of the problem that causes much of the confusion can be summarized in a single – somewhat surprising – sentence: it is of limited practical importance whether valid or unjustified relations are used – usually both of them result in similar kinetic parameters. Eq. (3) is used under non-isothermal conditions  $T = T_0 + Qt$  in ref. [1] to determine  $E$  and  $n$ . The result is

$$\frac{1}{n} \ln[- \ln(1-X)] = \ln \frac{K_0}{Q} - \frac{E}{RT} + \ln(T - T_0). \quad (7^*)$$

If the conventional treatment of thermal analysis is applied then the rate equation [eq. (6)] is integrated to yield eq. (5). [In the simple case investigated here eq. (5) is an exact result [6–8], otherwise it is only an approximation.] For a linear temperature program,  $T = T_0 + Qt$  and eq. (4) as the rate factor, eq. (5) is rewritten as

$$[- \ln(1-X)]^{1/n} = \frac{K_0 E}{RQ} \int_{E/RT}^{\infty} e^{-E/RT} \frac{d(E/RT)}{(E/RT)^2}. \quad (5')$$

The integral on the right-hand side is denoted by  $P(E/RT)$  and it is approximated as in ref. [1]:

$$\alpha, \ln P(E/RT) \approx -5.33 - 1.05E/RT,$$

$$\beta, \ln P(E/RT) \approx -E/RT - 2 \ln(E/RT).$$

The equations for the transformed fraction are

$$\frac{1}{n} \ln[- \ln(1-X)] = \ln(K_0 E / QR) - 5.33 - 1.05E/RT, \quad (7\alpha)$$

$$\frac{1}{n} \ln[- \ln(1-X)] = \ln(K_0 E / QR) - E/RT - 2 \ln(E/RT). \quad (7\beta)$$

It is obvious that for the effective and reliable multiple scan methods of thermal analysis [26]:

$$\left. \frac{d \ln[- \ln(1-X)]}{d \ln Q} \right|_T = -n,$$

$$\left. \frac{d \ln Q}{d(1/T)} \right|_X \approx -E/R,$$

it is of little importance whether the unjustified (7\*) or the widely used approximations (7 $\alpha$ ) and (7 $\beta$ ) are valid. The difference is of the order of  $\ln T$ , the change of which is usually negligible. This is the same reason why  $E$  and  $n$  cannot be determined simultaneously from a single thermal scan [8,27]: if  $\ln[-\ln(1-X)]$  is plotted versus  $1/T$  the deviation from linearity is negligible and the slope is  $-nE/R$ .

The basic reason for this strange behaviour is clear. The notoriously steep temperature dependence of the rate factor [eq. (4)] is capable of masking any slowly changing factors. This is why the leading term of any (good or unjustified) approximations might yield the same results within the limits of experimental error.

The difference between rate equations (6) and (6\*) is however observed when the transformation rate measured under non-isothermal conditions is compared with calculated curves. The transformation rate of  $\text{Fe}_{75}\text{B}_{25}$  metallic glass measured at 10 K/min heating rate is shown in fig. 2 (full circles) together with three calculated curves. The kinetic parameters have been determined [16] by a series of isothermal and dynamic measurements. Crosses

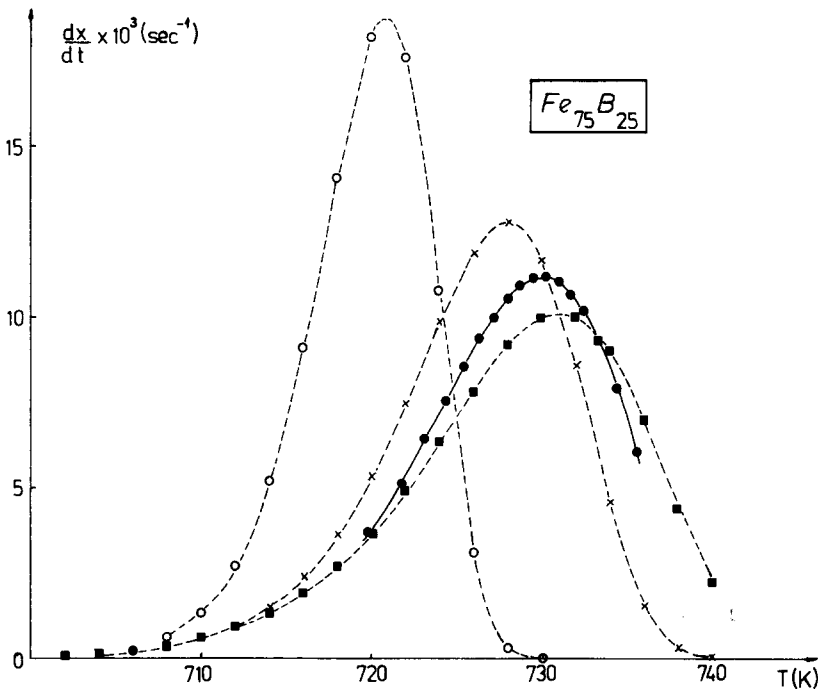


Fig. 2. The measured crystallization rate (full circles) is compared with that calculated by eq. (6) using the kinetic parameters determined from dynamic (full squares) and isothermal (crosses) measurements. Eq. (6\*) yields the curve denoted by empty circles.

and full squares denote the transformation rate curves calculated from these kinetic parameters respectively using eq. (6). Taking into account statistical and systematic errors the three curves are in acceptable agreement. When eq. (6\*) is applied the curve denoted by empty circles is obtained. It is clear that the significant acceleration of crystallization under non-isothermal conditions which is predicted by eq. (6\*) is not observed.

### 3. The general problem of non-isothermal investigations

It is not widely recognized in the literature dealing with crystallization kinetics that the question whether eq. (6) or eq. (6\*) is the correct rate equation under non-isothermal conditions is common to all of the problems investigated by thermal analysis. If the transformed fraction were a state function of its variables  $X = X[t, T(t)]$  then a general correction would result in the rate equation of *any* transformation or reaction under non-isothermal conditions.

The usual approach of thermal analysis is based on a kind of rational extension of the isothermal law

$$g(X) = K(T)t. \quad (5G/I)$$

In a short time interval  $\Delta t$ , the change under isothermal conditions is

$$\Delta g_T(X) = K(T)\Delta t. \quad (6G/I)$$

An evident approximation for the case when temperature is also changed via  $T(t)$  is the use of the same relation, eq. (6G/I) for the change  $\Delta g_{(T, T+\Delta T)}(t, t + \Delta t)$ . This assumption is the isokinetic hypothesis: the rate of a process is uniquely determined by the actual temperature and the transformed fraction. In this way, as  $g(X=0) = 0$ ;

$$g(X) = \lim_{n \rightarrow \infty} \sum_{i=1}^n \Delta g_{(T, T+\Delta T)}(t_i, t_i + \Delta t).$$

Thus one obtains

$$g(X) = \int_0^t K[T(t')] dt'. \quad (5G)$$

Its derivative yields

$$dX/dt = f(X)K(T) \quad (6G)$$

where

$$f(X) = (dg/dX)^{-1}.$$

The importance of the remark of Henderson [6,7] is to be understood in this context. He has drawn attention to the fact that the reasoning given above is not exactly valid. The formal theory of transformations [i.e. eq. (1)] is not generally isokinetic.

The consequences of this fact were investigated by De Bruijn et al. [8]. Their

solution for the simplest case (the growth of a fixed number of nuclei) has already been utilized in eqs. (5) and (6). It was also shown in ref. [8] that the temperature dependence of eq. (1) is similar in form to eq. (5G) when both nucleation and growth occur simultaneously. In this way the same activation energy and characteristic exponent can in principle be determined from isothermal and dynamic investigations with only the frequency factor  $K_0$ , being somewhat changed.

The usual practice of thermal analysis is thus based on two assumptions:

- (1) The transformed fraction is *not* a state function of its variable,  $t$  and  $T$ , as it is also dependent on the  $T(t)$  path.
- (2) The isokinetic hypothesis is a fair approximation, i.e. the same rate equation is valid for *any*  $T(t)$  path, including the  $T = T_0$  isotherms.

An alternative formulation is sometimes suggested [5,9,10] which is based on the assumption that  $X = X[t, T(t)]$  is a state function of its variables. The rate equation is calculated [9,10] via

$$\frac{dX}{dt} = \left. \frac{\partial X}{\partial t} \right|_T + \left. \frac{\partial X}{\partial T} \right|_t \frac{dT}{dt} \quad (9^*G)$$

by analysing the partial derivatives. The result is of the same form as eq. (6\*)

$$\frac{dX}{dt} = F(X)K(T) \left( 1 + \frac{T - T_0}{T^2} \frac{E}{R} \right). \quad (6^*G)$$

Using the basic assumption  $X = X[t, T(t)]$  this derivative can however be calculated in a much simpler way – namely from the isothermal law. Once the existence of a state function  $X = X[t, T(t)]$  is accepted its value is naturally independent of whether the point  $(T, t)$  is reached isothermally or via any complicated  $T(t)$  path.

The isothermal law reads as

$$g(X) = K(T)t \quad (5G/I)$$

its isothermal derivative is

$$dX/dt = f(X)K(T),$$

where

$$f(X) = (dg/dX)^{-1}.$$

The time derivative of eq. (5G/I) for the linear temperature program  $T = T_0 + Qt$  yields eq. (6\*G).

The implications of this alternative formulation must however be understood:

- (a) The transformed fraction would be a state function of time and temperature only, it is independent of the  $T(t)$  path.
- (b) The rate of the processes corresponding to this behaviour should be significantly higher under non-isothermal conditions than that calculated by eq. (6G).

If some processes correspond to this alternative formulation they are easily

revealed by a comparison of the isothermal and dynamic measurements. A detailed investigation has been carried out by Koch et al. [13] for a wide range of chemical reactions. Their finding is in sound agreement with our crystallization studies: the non-isothermal transformation rate must be described by eq. (6G) and the modified rate equation of the alternative formulation, eq. (6\*G), is not applicable to any known case.

#### 4. Conclusion

The alternative formulation of thermal analysis based on the existence of an  $X[t, T(t)]$  state function and a modified rate equation, eq. (6\*G), under non-isothermal conditions is generally expected to be unjustified on logical grounds [11–15] and is even contradicted by direct experimental results in some cases [11,13,16]. It cannot however be proven that it is *a priori* invalid for any processes. The crystallization kinetics on the other hand belongs to those cases where no doubts can be raised. The formal theory of transformation kinetics, i.e. eq. (1), is incompatible with the alternative hypothesis – as is clearly shown in refs. [6–8].

The treatment of non-isothermal crystallization kinetics must be refined along the lines suggested in refs. [6–8]. Yinnon and Uhlmann are undoubtedly right when they point out the limitations inherent in the use of an Arrhenian rate factor and in restricting ourselves to analytical methods. Their view that there is much to be gained from a correct numerical description of transformation kinetics can hardly be doubted.

The general correction of ref. [1] is however misleading since there is neither experimental support nor theoretical justification for using eq. (6\*) (that is eq. (15) of ref. [1]) as the rate equation in non-isothermal studies of crystallization kinetics.

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#### Appendix

$$T^{(1)}(t) = T_0 + Qt \text{ where } Q = \frac{T_1 - T_0}{t_1}, \quad (\text{A/1})$$

$$T^{(2)}(t) = \frac{T_0}{1 - bt} \text{ where } b = \frac{T_1 - T_0}{t_1 T_1}. \quad (\text{A/2})$$

The requirements that

$$T^{(1)}(t) > T^{(2)}(t) \text{ for } 0 < t < t_1$$

and  $T^{(1)}(t_1) = T^{(2)}(t_1) = T_1$  are obviously fulfilled. For the linear program



(A/1) the approximation (7 $\beta$ ) is used. The exponential integral can be treated analytically for the hyperbolic program (A/2), thus eq. (5) yields

$$\left[-\ln(1 - X_1^{(2)})\right]^{1/n} = -\frac{K_0 T_0 R}{bE} \int_0^{T_1} e^{-E/RT} d(E/RT). \quad (\text{A/3})$$

When  $Q$  and  $b$  are inserted from eqs. (A/1) and (A/2) into eqs (7 $\beta$ ) and (A/3) respectively, their difference yields:

$$\begin{aligned} \Delta &= \frac{1}{n} \left( \ln \ln \frac{1}{1 - X_1^{(1)}} - \ln \ln \frac{1}{1 - X_1^{(2)}} \right) \\ &= \ln \frac{\frac{E}{R} \frac{t_1}{T_1 - T_0}}{\left(\frac{E}{RT_1}\right)^2 \frac{RT_0}{E} \frac{T_1 t_1}{T_1 - T_0}} = \ln(T_1/T_0) > 0. \end{aligned}$$

Hence  $X_1^{(1)} > X_1^{(2)}$  is verified.

*Note added in proof:* Since the submission of this paper we have become aware of some new results supporting our conclusion. Meisel and Cote show [28] that the alternative formulation, where the transformed fraction is a state function, leads to absurd results when applied to crystallization kinetics. The same view, expressed earlier by Tang and Chaudhri [15] is reiterated in a recent work of Tang [29] who also gives [30] a sound criticism of some papers [31,32] where transformed fraction is treated as a state function of its variables.

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