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# Decomposition of solids accompanied by melting—Bawn kinetics

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## Abstract

The book "Chemistry of the Solid State", edited by W.E. Garner more than 50 years ago, contained a chapter (Chapter 10) by C.E.H. Bawn which dealt with the kinetics of the thermal decompositions of solids that are accompanied by some melting. Rate equations were derived and this model has become known as the Bawn model or as "Bawn kinetics". This kinetic model has proved particularly useful in pharmaceutical stability studies. The isothermal curves of extent of decomposition, $\alpha$, against time for this model are sigmoidal and the problems of distinguishing this model from other sigmoidal models (Prout–Tompkins, Avrami–Erofeev) have been examined. Under programmed temperature conditions, distinguishability becomes even more difficult.

*Keywords:* Kinetics; Bawn model; Sigmoidal models; Melting and decomposition; Stability

## 1. Introduction

The book "Chemistry of the Solid State", edited by W.E. Garner almost 50 years ago, contained a chapter (Chapter 10) by C.E.H. Bawn (Bawn, 1955)[1] which dealt with the kinetics of the thermal decompositions of solids that are accompanied by some melting. Rate equations were derived and this model has become known as the Bawn model or as "Bawn kinetics". Attempts to trace the origin of these rate equations in earlier papers by Bawn were not successful. Very few of the articles that cite the Bawn chapter actually apply the kinetic model. Most citations are as a general reference to the thermal decomposition of organic solids and/or to the decompositions of organic explosives. Amongst the decompositions of organic solids to which Bawn kinetics have been applied, those of pharmaceuticals have featured prominently.

## 2. Rate equations in solid-state kinetics

The rate equations that have found application in solid-state kinetic analyses (Brown et al., 1980; Galwey and Brown, 1999) may be generalised in their derivative forms as: $\mathrm{d}\alpha/\mathrm{d}t = kf(\alpha)$ and the corresponding integrated forms as: $g(\alpha) = kt + c$, where $\alpha$ is the fractional extent of reaction. These expressions are grouped according to the shape of the *isothermal* $\alpha$–time curves as acceleratory, sigmoid or deceleratory (Brown et al., 1980; Galwey and Brown, 1999). The Bawn model (Bawn, 1955), because it is

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[1] Emeritus Professor Cecil Edwin Henry Bawn, B.Sc., Ph.D. (Bristol), CBE (1956), FRS (1952), was Brummer Professor of Inorganic and Physical Chemistry at the University of Liverpool until his retirement in 1969. He is also widely known for his book "The Chemistry of High Polymers", Butterworths, London, 1948.

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not strictly applicable to decompositions occurring entirely in the solid state, does not usually appear in this classification.

As a consequence of the bonding in and, hence, the crystal structures of organic solids, melting or sublimation may be expected to precede or accompany thermal decomposition. Galwey (1995a,b) has discussed the possible role of melting in thermal reactions of initially solid reactants, which is not always considered in the interpretation of kinetic data and the formulation of reaction mechanisms. Formation of a liquid phase may result in increased rates of isothermal decomposition and produce sigmoid $\alpha$–time curves.

Carstensen (1995) has done much to promote consideration of the Bawn model, particularly in studies of the decompositions of pharmaceuticals. The Bawn model applies to the situation where reactant A is soluble in product B with solubility, $s$. When the extent of decomposition is $\alpha$, the fraction of A in the liquid phase is $\alpha s$, and in the solid phase is $(1-\alpha-\alpha s)$. If the rate coefficients for reactions in the solid and in the liquid phases are $k_s$ and $k_l$, respectively, then:

$$\frac{d\alpha}{dt} = k_s(1-\alpha-\alpha s) + k_l\alpha s = k_s + K\alpha \tag{1}$$

where $K = k_l s - k_s s - k_s$, and

$$\alpha = \left(\frac{k_s}{K}\right)[\exp(Kt) - 1] \tag{2}$$

The expected ratio $k_l/k_s$ can be estimated (Carstensen, 1995), as follows. Using:

$$k_s = A_s \exp\left(\frac{-E_s}{RT}\right) \quad \text{and} \quad k_l = A_l \exp\left(\frac{-E_l}{RT}\right)$$

and assuming that the difference $E_s - E_l$ is equal to the molar enthalpy of melting, then if $A_s \approx A_l$:

$$\frac{k_l}{k_s} \approx \exp\left(\frac{\Delta H_{\text{melting}}}{RT}\right)$$

For a typical value of $\Delta H_{\text{melting}} \approx 20\,\text{kJ mol}^{-1}$ and $T = 400\,\text{K}$, $k_l/k_s \approx 410$.

The $\alpha$–time curves for the Bawn model are sigmoidal, being acceleratory according to Eq. (2), up to the liquefaction point, where $\alpha = \alpha^* = 1/(1+s)$ at $t = t^*$, and deceleratory beyond according to:

$$\frac{1-\alpha}{1-\alpha^*} = \exp[-k_l(t-t^*)] \tag{3}$$

## 3. Distinguishability from other sigmoid models

Establishing which of the alternative kinetic expressions best describes sets of experimental data is difficult (Brown and Galwey, 1979; Galwey and Brown, 1995) and a subject of endless discussion (Brown et al., 2000). The conventional sigmoid expressions, the Prout–Tompkins equation (often referred to as B1) and the Johnson–Mehl–Avrami–Erofeev–Kholmogorov (JMAEK) equation (referred to as A$n$) are difficult to distinguish clearly if the exponent $n$ is allowed to assume any value, including non-integer values. The Sesták–Berggren equation was proposed (Sesták and Berggren, 1971; Ng, 1975; Malek and Criado, 1991) to include most of the familiar rate equations:

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n(-\ln(1-\alpha))^p \tag{4}$$

When $m = p = 0$, the general equation becomes the “reaction order” (RO) model with a variety of shapes of deceleratory $\alpha$–time curves depending on the value of $n$ (which is not restricted to integer values). When $m = n = 1$ and $p = 0$, the Prout–Tompkins equation results (Brown, 1997; Brown and Glass, 1999), and when $m = n = 0$, the general equation becomes the JMAEK equation (usually written with $p = n$).

This paper explores the distinguishability of the Bawn rate equations from the other solid-state sigmoid models under isothermal conditions and discusses the greater difficulties expected under programmed temperature conditions.

## 4. Application of the Bawn model

To test whether a set of *isothermal* $\alpha$–time data can be satisfactorily described by the Bawn model, the coordinates of the point of inflection, $t^*$ and $\alpha^*$ are determined. The value of $\alpha^*$ enables the solubility parameter, $s = (1-\alpha^*)/\alpha^*$ to be calculated. To estimate the value for the ratio, $k_l/k_s$, it is convenient to combine parameters so that:

$$B = \frac{K}{k_s} = \frac{k_l}{k_s}s - s - 1 \tag{5}$$

Data for the acceleratory period $(0 < \alpha < \alpha^*)$ are then fitted to:

$$\ln[1 + B\alpha] = Bk_s t \tag{6}$$

by adjustment of $B$. When $t = 0$, $\alpha = 0$, so the plot should pass through the origin. The slope of this plot, for the optimum value of $B$, leads to a value for $k_s$. These values, used in Eq. (5) give a value of $k_l$.

The deceleratory part of the curve ($\alpha^* < \alpha < 1.0$) is then examined by plotting:

$$\ln\left(\frac{1-\alpha}{1-\alpha^*}\right) \quad \text{against} \quad (t-t^*)$$

(see Eq. (3)) and the slope gives a value for $k_l$ which is independent of the value of $B$ and can be compared with the value found for the acceleratory period.

It is necessary to explore the influences of the somewhat interdependent adjustable parameters in the Bawn model. The only significance of $t^*$ will be in relation to the absolute values of the rate coefficients, $k_l$ and $k_s$. It is advantageous to use a reduced-time scale such that $t^* = 1.00$ at $\alpha = \alpha^*$. The value of $\alpha^*$ is determined by the solubility parameter $s\ (= (1-\alpha^*)/\alpha^*)$. $\alpha^*$ can range from 0 to 1. It would be expected that $s$ (moles of reactant dissolved per mole of liquid product) is unlikely to be a large number, so $\alpha^*$ is likely to be in the mid range and the ratio $k_l/k_s$ can reasonably be assumed to be greater than 1.

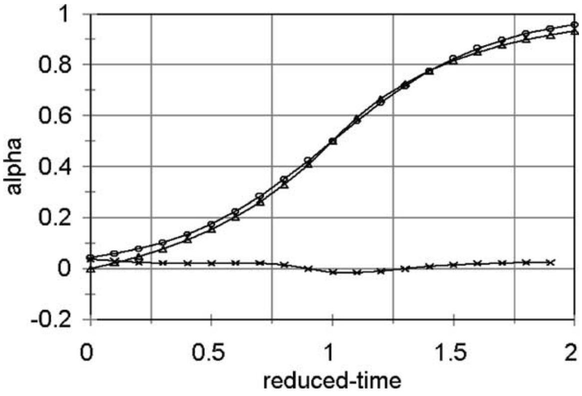

Fig. 1. The isothermal $\alpha$–reduced-time curve (△) for the Bawn model with $\alpha^* = 0.50$ and $t^* = 1.00$, $k_l/k_s = 10$ and $s = 1$. Curve (○) is the closest fit of the Prout–Tompkins model with $k = 3.10 \pm 0.07$. Curve (×) is a plot of the residuals (alpha PT–alpha Bawn).

For $k_l/k_s = 10$

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $\alpha^*$ | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
| $s$ | 9 | 4 | 2.33 | 1.5 | 1 | 0.667 | 0.429 | 0.25 | 0.111 |
| $B$ | 80 | 35 | 20 | 12.5 | 8 | 5 | 2.86 | 1.25 | −3.33E−16 |
| $k_s$ | 0.0274 | 0.0594 | 0.0973 | 0.1433 | 0.2012 | 0.2773 | 0.3845 | 0.5545 | 1 |
| $k_l$ | 0.2747 | 0.5941 | 0.9730 | 1.433 | 2.012 | 2.773 | 3.845 | 5.545 | 10 |

As a reference set of data for comparative purposes, the Bawn model was used to calculate a set of isothermal $\alpha$–time data such that $\alpha^* = 0.50$ and $t^* = 1.00$, with $k_l/k_s = 10$ and $s = 1$. This requires that $B = 8$ and $k_s (= (\ln(1 + B\alpha^*)/Bt^*) = 0.201$. $k_l = 10k_s = 2.01$. The $\alpha$–time curve is illustrated in Fig. 1.

These parameters give a smooth and reasonably symmetrical sigmoid curve that could readily be confused with other sigmoid models (Brown et al., 1980; Galwey and Brown, 1999). For example, the Prout–Tompkins equation has been used quite extensively in the kinetic analysis of reactions of pharmaceutical interest [14]. To test the Bawn model, the early stages of decomposition should give a linear plot of ln $\alpha$ against $t$ and the later stages a linear plot of $\ln(1-\alpha)$ against $t$. The same holds for the PT model, so the two models cannot readily be distinguished on kinetic grounds.

Two less-symmetrical examples are shown in Fig. 2, for $\alpha^* = 0.30$ and 0.70 and the interdependent parameters.

The reverse of the above procedure involved applying the Bawn analysis to data calculated for the PT equation. The results (not illustrated) for PT data, calculated for a single $k_{PT}$ value of 3.892 to give $\alpha^* = 0.50$ and $t^* = 1.00$, resulted in coincidence of the Bawn curve with the original data of the order of that shown in Fig. 1, if $B = 57$, $s = 1$, $k_s = 0.0478$, $k_l = 2.82$ (acceleratory period) or 3.27 (deceleratory region).

The Bawn analysis procedure was also used on a set of isothermal $\alpha$–reduced-time data calculated for the JMAEK model (Brown et al., 1980; Galwey and Brown, 1999) with $n = 3$ (the A3 model) and with $\alpha^* = 0.50$ and $t^* = 1.0$, i.e. $\alpha = 1 - \exp(-k_3 t)^3$ with $k_3 = 0.8850$. Determination of an optimum value of parameter $B$ from the acceleratory period of the A3

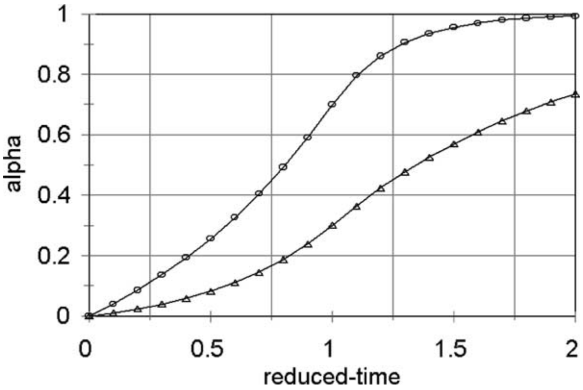

Fig. 2. Isothermal $\alpha$–reduced-time curves for the Bawn model (△) with $\alpha^* = 0.30$ and $t^* = 1.00$, $k_l/k_s = 10$ and $s = 2.33$, $B = 20$, $k_s = 0.0973$, $k_l = 0.973$; and (○) with $\alpha^* = 0.70$ and $t^* = 1.00$, $k_l/k_s = 10$ and $s = 0.43$, $B = 2.86$, $k_s = 0.3845$, $k_l = 3.845$.

curve shown in Fig. 3 gave poor linearity with the highest $r^2$ value (0.9844) $B = 60$ ($k_s = 0.0644$ and $k_l = 3.99$) but a non-zero intercept (−0.24). For a zero intercept, the $r^2$ value decreased to 0.9730 and $B = 204$ ($k_s = 0.0249$ and $k_l = 5.13$), see Fig. 4.

Analysis of the deceleratory region again gave poor linearity, see Fig. 5, with $r^2 = 0.9680$ and $k_l = 4.80 \pm 0.29$ lying between the values estimated from the acceleratory period (Fig. 4).

Returning to the Bawn model as represented in Fig. 1, analysis in terms of the JMAEK models with $n = 2$–4 led to the recalculated $\alpha$–time curves shown in Fig. 6. Distinguishability is poor but can be improved slightly by examining the residuals ($\alpha_{\text{expt}} - \alpha_{\text{calc}}$) (Brown and Galwey, 1979) shown in Fig. 7.

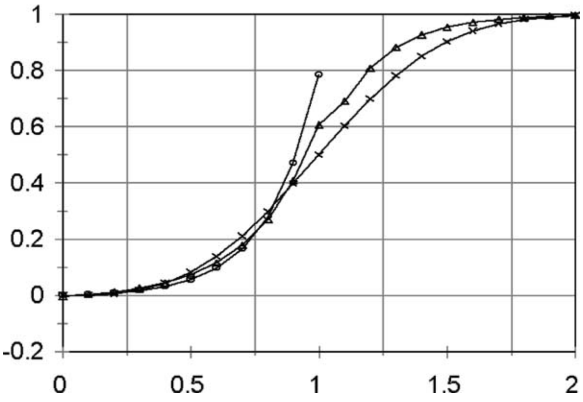

Fig. 3. An isothermal $\alpha$–reduced-time curve (×) calculated for the JMAEK model with $n = 3$ (the A3 model) and with $\alpha^* = 0.50$ and $t^* = 1.0$, i.e. $\alpha = 1 - \exp(-k_3 t)^3$ with $k_3 = 0.8850$. The superimposed curves are the calculated curves from a Bawn analysis of the A3 data over the acceleratory and deceleratory regions. Curve (△) is $B = 60$ and curve (○) is $B = 204$, see Fig. 4.

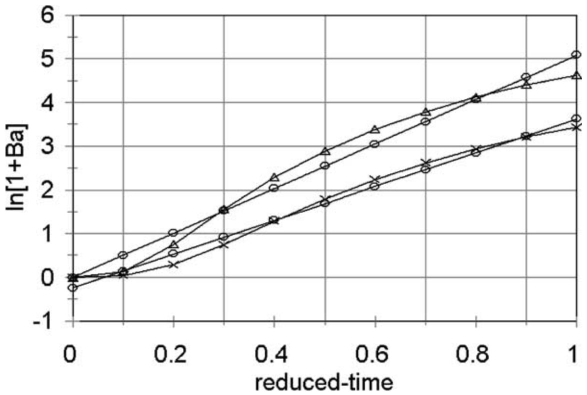

Fig. 4. Bawn analysis of the acceleratory period of the A3 curve shown in Fig. 3, together with regression lines (○). The highest $r^2$ value (0.9844) was obtained for $B = 60$ (×) ($k_s = 0.0644$ and $k_l = 3.99$) but a non-zero intercept (−0.24). For a zero intercept (△), the $r^2$ value decreased to 0.9730 and $B = 204$ ($k_s = 0.0249$ and $k_l = 5.13$).

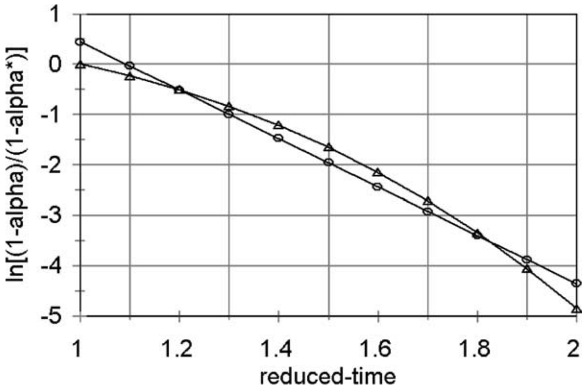

Fig. 5. Bawn analysis (△) of the deceleratory region of the A3 model (Fig. 3). $r^2 = 0.9680$ and $k_l = 4.80 \pm 0.29$, together with the regression line (○).

## 5. The generalized Prout–Tompkins equation

Jacobs (1997) has re-examined the Prout–Tompkins model and generalized it for application to non-symmetrical isothermal $\alpha$–time curves. Carstensen

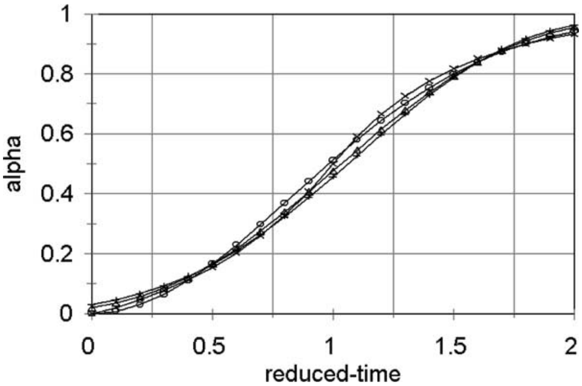

Fig. 6. JMAEK analysis of the Bawn model from Fig. 1. (×) Bawn curve; (○) A2 model ($k = 0.842 \pm 0.014$); (△) A3 model ($k = 0.597 \pm 0.014$); (+) A4 model ($k = 0.465 \pm 0.014$).

(1980) has provided a mathematically more-complex alternative treatment that is more difficult to apply and interpret. Jacob's (1997) treatment results in the following expression for $\alpha$:

$$\alpha = \left[(\exp(k(t - t_o) + C)^{-1} + \left(\frac{1}{2}\alpha_i\right)\right]^{-1}$$

where $C = \alpha_o/(1 - \alpha_o/2\alpha_i)$ and $\alpha_o$ is the extent of initial decomposition that takes place in the time interval, $0 < t < t_o$, before the PT mechanism applies. $\alpha_i$ is the value of $\alpha$ at the point of inflection. A set of $\alpha$–time data calculated for a symmetrical Bawn model ($\alpha^* = 0.50$, $t^* = 1.00$, $s = 1$, $B = 8$, $k_s = 0.20118$, $k_l = 2.0118$) was analyzed using the non-linear regression program, NLREG (Sherrod Software), to determine the parameters $t_o$, $\alpha_o$, $\alpha_i$. The result was that the curve could be adequately described using $t_o = 0.9778 \pm 0.0019$; $\alpha_i = 0.4769 \pm 0.0013$, $\alpha_o = -0.0228 \pm 0.0030$, and a single rate constant $k = 3.405 \pm 0.034$.

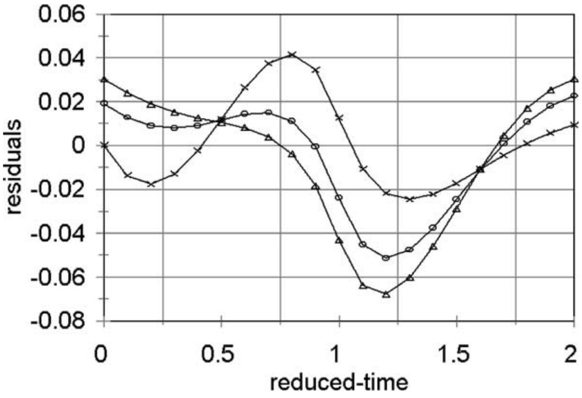

Fig. 7. Residual plots ($\alpha_{\text{expt}} - \alpha_{\text{calc}}$) for Fig. 6. (×) A2 model; (○) A3 model; (△) A4 model.

## 6. Effect of temperature

Isothermal experiments will fall into two broad groups depending upon whether the temperature is below or above the minimum required for partial liquefaction of the reactant/product mixture. This minimum temperature, in turn, depends upon the extent of decomposition, because, assuming that Raoult's law applies (Bawn, 1955), the proportion of product will determine the lowering of the normal melting point of the reactant. Bawn (1955) quotes an example of a study (Yoffe, 1951) on the decomposition of trinitrotriazidobenzene. The normal melting point of the reactant was 130 °C. Below the melting point, decomposition (giving nitrogen and hexanitrosobenzene, melting point 15 °C) was slow, but if the solid was maintained at 120 °C, melting occurred after 6 min, and decomposition became rapid. Decomposition of molten Tetryl (Hinshelwood, 1921) was about 50 times greater than in the solid state just below the melting point. Addition of substances that lowered the melting point, increased the rate of decomposition. Addition of picric acid, which is a decomposition product, increased the rate of decomposition in both the solid and liquid states, so autocatalysis also plays a part.

Carstensen and Musa (1972) used the Bawn model in describing their results for the decomposition of a series of substituted benzoic acids. The decomposition of *m*-nitroperoxybenzoic acid (Debenham and Owen, 1966) proceeds entirely in the solid phase at 66.5 °C, but at temperatures up to 90 °C the reactant melts at some stage of the decomposition. The PT expression was used to describe the symmetrical sigmoid $\alpha$–time curves obtained. The fact that the reactant melts invalidates the PT model, but autocatalysis of the decomposition by *m*-nitrobenzoic acid, the principal product of decomposition, was shown to occur. Addition of other substituted benzoic acids to the reactant also catalysed decomposition.

## 7. Non-isothermal Bawn kinetics

From the discussion of the effect of temperature, above, the behaviour of the Bawn model under programmed temperature experiments can be expected to be very complicated. For two concurrent processes (Vyazovkin and Lesnikovich, 1990, Criado et al., 1988) with constant contributions $w_1$ and $w_2$ of the overall reaction and different Arrhenius parameters, separation of the contributions is most easily achieved when the activation energies of the two processes are considerably different. Processes with low $E_a$ values dominate the kinetics at low temperatures and slow heating rates, while processes with high $E_a$ values dominate at high temperatures and fast heating rates.

## 8. The Bawn model

The nature and coordinates of the inflection point, $t^*$ and $\alpha^*$, are the important criteria in judging the possible applicability of the Bawn model. If the inflection is very marked (worse than the behaviour illustrated in Fig. 2) complex kinetics would be clearly indicated and the Bawn model is one specific instance of the range of concurrent/consecutive complex mechanisms. It is fairly generally recognised (Brown et al., 2000) that isothermal experiments are more successful in identifying kinetic models, while programmed temperature experiments provide more accurate information on the Arrhenius parameters and their possible variation with extent of reaction.

For smoother inflection points, the isothermal $\alpha$–time curves calculated from appropriate sets of input parameters for the Bawn model are not readily distinguishable from curves calculated, usually with fewer adjustable parameters, for the other, better known, sigmoidal models.

The solubility parameter, $s = (1 - \alpha^*)/\alpha^*$ does not appear to be readily measurable in a direct experiment and thus, becomes simply a parameter that is dependent on $\alpha^*$. The parameter $B = (k_l/k_s) - s - 1$ contains the ratio of rate constants, $k_l/k_s$, and is thus generally going to be strongly temperature dependent. $B$ is the main adjustable parameter in the curve fitting of the acceleratory period and leads to a value for $k_s$. Combination with the adjusted value of $B$ gives a value of $k_l$. The deceleratory part of the curve gives a value for $k_l$ which is independent of the value of $B$ and can be compared with the value found for the acceleratory period. Agreement between the two estimates of $k_l$ is not very impressive.

Apparent applicability of the Bawn model to experimental data, like all such kinetic analyses, does not prove the occurrence of the mechanism on which the model is based. In this instance, there are at least three possible explanations. The observed acceleratory effect may be the result of partial melting, or of autocatalysis, (or both), or be describable by other sigmoid models.

Pharmaceutical studies of stability are generally concerned mainly with initial degradation. Information is usually required on the degradation of the drug alone, on mixing with excipients, and in the presence of moisture. Accelerated degradation studies have to be extrapolated to lower temperatures, with allowance for the possibility of phase changes, and taking the estimated errors in the kinetic parameters ($E_a$, $A$ and $g(\alpha)$) into account. It is quite possible for studies to be conducted at isothermal temperatures where the time taken, $t^*$, to reach the critical value of the fractional decomposition, $\alpha^*$, may be greater than that reasonably available, and the possible contribution from later melting may be overlooked. It is, thus, necessary to explore a range of isothermal temperatures, as well as the information available from conventional thermal analysis (DSC, TG) experiments, when deciding that the Bawn model could be applicable under certain conditions. When the degradation curves are deceleratory overall, assumption of zero-order behaviour in the early stages of reaction is reasonable, but this is not acceptable for sigmoidal $\alpha$–time curves. If, as is commonly found, reaction in the melt is more rapid than in the solid state, extrapolation of observed behaviour to expected behaviour at lower temperatures will be invalid.

## 9. Conclusions

The Bawn model is an attempt to account quantitatively for the occurrence of significant amounts of melting during decomposition of a solid. Like all kinetic analyses though, the applicability of the model has to be supported by additional evidence. Use of modulated temperature DSC to separate melting (reversible) from decomposition (irreversible) is perhaps the most promising technique.

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