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A COMMENT ON MATHEMATICAL EXPRESSIONS USED IN SOLID STATE REACTION KINETICS STUDIES BY THERMAL ANALYSIS

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ABSTRACT

Computer calculations pertaining to the reaction kinetics analyses of simulated thermoanalytical data, generated under non-isothermal conditions, have been performed. Results obtained by using the two forms of the differential and integral equations descriptive of three different models of rate-controlled solid state reactions: phase boundary movement, nucleation-growth and three-dimensional diffusion, have been examined and compared. Calculations have also been performed to examine the correctness of employing the simple diffusion model equations to analyze data generated by taking into consideration differences in the density of reactant and product. For all models studied and compared, the activation energies are the same, but the pre-exponential factors differ slightly. They can be interconverted by the use of an appropriate multiplicative constant.

INTRODUCTION

In carrying out computer modelling studies of multiple solid state reactions, I have had occasion to inquire into the correctness of certain mathematical expressions, descriptive of various rate-controlling phenomena, used in generating the reaction kinetics parameters, activation energy and pre-exponential factor from thermoanalytical data. Since there are differences and, it appears, errors in the multiplicative coefficients of a number of equations appearing in the literature, it was decided to collate this information, and to examine the effects of using these different values in the analysis of simulated non-isothermally derived data. Specifically, the differences are associated with the equations describing nucleation-growth phenomena, phase boundary movement and three-dimensional diffusion in solid state reactions. With regard to the latter phenomena, it was further decided to examine the effect of using the simple expressions to analyze simulated data generated by equations which take into account differences in the molar volume of reactant and product. This paper will summarize the results of several computer calculations and, hopefully, dispel any confusion within the thermoanalytical community.

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THEORETICAL RELATIONSHIPS

The rate of a thermally simulated solid state reaction is usually expressed in terms of the dimensionless extent of reaction, α, by eqn. (1), with the temperature dependent rate constant given by eqn. (2). The extent of reaction is obtained from the integral form, $g(\alpha)$, of the $f(\alpha)$ function by eqn. (3).

$$\mathrm{d}\alpha/\mathrm{d}t = k_T f(\alpha) \tag{1}$$

$$k_T = AT^m \exp(-E/RT) \tag{2}$$

$$g(\alpha) = \int_0^{\alpha} \mathrm{d}\alpha/f(\alpha) \tag{3}$$

Generally, the temperature exponent, m, of the pre-exponential factor is set equal to zero, and (2) is referred to as the Arrhenius equation. This is the procedure which will be followed here.

Table 1 summarizes the expressions for $f(\alpha)$ and $g(\alpha)$ for the models which show discrepancies. Three sets of values of the multiplicative coefficients k_1 and k_2 have been given; see Brown et al. [1] and Šesták [2] for details. As may be quickly verified, both form 1 and form 2 coefficients satisfy eqn. (3) Even though Šesták [2a] discusses the various form 1 $g(\alpha)$ functions, with one exception, namely the Jander model, D3, the form 3 expressions tabulated in his appendix [2b] do not obey this relationship. The reader should be aware of these errors, even though obviously typographical.

Before surveying the use of forms 1 and 2 in the recent literature, it is pertinent to consider a special case, the Avrami–Erofeev model. The general expression for the extent of reaction, given by Erofeev [3], is

$$\alpha = 1 - \exp(-k_\mathrm{E} t^n) \tag{4}$$

However, it may easily be shown, as already indicated by Fatemi et al. [4], the rate constant $k_\mathrm{E} = k_T^n$. Thus, from the Arrhenius equation (2), the correct values of the activation energy and pre-exponential factor are

$$A_\mathrm{E} = A^n \tag{5a}$$

$$E_\mathrm{E} = nE \tag{5b}$$

Khanna and Taylor [5] have also used these equations in calculating Avrami–Erofeev reaction kinetics parameters from isothermal DSC data characterizing the crystallization of various nylons. Taylor and Khanna [6] have discussed this point further, and used form 2 $g(\alpha)$ functions in their computerized analysis of non-isothermal DSC and TG data characterizing the thermal degradation of polystyrene and polyamide.

The form 1 expressions [1(a)] are in accord with those discussed by Sharp et al. [7] and Heide et al. [8], and, in the main, are those used by most investigators. In the area of thermal degradation studies by TG, Bhatti et al.

TABLE 1

Kinetics mechanistic models

Mechanistic model		Integral equation $g(\alpha)$	Differential equation $f(\alpha)$	Form 1 [1a]		Form 2 [1b]		Form 3 [2b]	
				k_1	k_2	k_1	k_2	k_1	k_2
Avrami–Erofeev	An [3]	$k_1[-\ln(1-\alpha)]^{1/n}$	$k_2(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$	1	n	n	1	$1-1/n$	1
	Rn [2]	$k_1[1-(1-\alpha)^{1/n}]$	$k_2(1-\alpha)^{1-1/n}$	1	n	n	1	$1-1/n$	1
Jander	D3 [9]	$k_1[1-(1-\alpha)^{1/3}]^2$	$k_2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	1	$\frac{3}{2}$	$\frac{3}{2}$	1	$\frac{3}{2}$	1
Gintsling–Brounshtein	D4 [9]	$k_1[1-2\alpha/3-(1-\alpha)^{2/3}]$	$k_2(1-\alpha)^{1/3}[1-(1-\alpha)^{1/3}]^{-1}$	1	$\frac{3}{2}$	$\frac{3}{2}$	1	$\frac{2}{3}$	1
Carter [10] ($Z>1$)	C	$k_1[Z-(Z\alpha+1-\alpha)^{2/3}]$ $-(1-\alpha)^{2/3}$	$k_2[(1-\alpha)^{-1/3}$ $-(Z\alpha+1-\alpha)^{-1/3}]^{-1}$	$\frac{1}{(Z-1)}$	$\frac{3}{2}$	–	–	–	–
anti-Jander [2]		$k_1[(1+\alpha)^{1/3}-1]^2$	$k_2(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	1	$\frac{3}{2}$	$\frac{3}{2}$	1	$\frac{2}{3}$	1
Zhuravlev [2]		$k_1[1-\alpha)^{-1/3}-1]^2$	$k_2(1-\alpha)^{4/3}[(1-\alpha)^{-1/3}-1]^{-1}$	1	$\frac{3}{2}$	$\frac{3}{2}$	1	$\frac{2}{3}$	1

[9], investigating the decomposition of acid barium oxalate by isothermal and non-isothermal means, employed form 1 An and Rn expressions. Bhatti et al. [10] analyzed the data for the isothermal degradation of anhydrous barium oxalate in terms of the form 1 An model, and found n values varying from 2 to 0.77. Similarly, Krishnan et al. [11], analyzing the isothermal data for the dehydration of zinc oxalate dihydrate, used form 1 An expressions and found n to decrease linearly with temperature. Nair and James [12], in studying the non-isothermal decomposition of strontium nitrate, employed a number of form 1 models, and found the Mampel equation, A1, mathematically equivalent to first order kinetics, F1, gave the best data correlation. DSC investigations of recrystallization phenomena in glassy materials have also employed form 1 expressions. Thus, Yardar et al. [13] found the isothermal recrystallization of polyvinylidene fluoride to follow an A3 mechanism. Lopez and Wilkes [14] investigated the recrystallization of poly(p-phenylene sulfide) by non-isothermal linear cooling studies. They too proposed an Avrami–Erofeev mechanism, and found n to increase slightly in the range 2–3 with increase in temperature. Málek [15], using multiple heating rate DSC, studied the recrystallization of germanium selenide glasses and analyzed the data in terms of a form 1 A3 model, and also as a second order mechanism.

In a few cases, form 2 expressions have been used to evaluate thermoanalytical data. Thus, Chou and Soong [16], studying the multi-stage dehydration of hydrated aluminum sulfate by multiple heating rate TG, employed a wide range of form 2 expressions to analyze their data. They found the best data correlation when the An model, with n either 1.5 or 2, was employed. Bhatti et al. [17] proposed a form 2 Zhuravlev [2] model for the dehydroxylation of magnesium hydroxide from non-isothermal DTA. Davies et al. [18] used a modified form 2 A4 model ($k_1 = 3$, $k_2 = 4/3$) to analyze DTA measurements of the transition kinetics in calcium carbonate polymorphs.

The use of form 2 expressions may derive from the general empirical expression proposed by Šesták and Berggren [19], namely

$$f(\alpha) = (1-\alpha)^p \alpha^q [-\ln(1-\alpha)]^r \tag{6}$$

At least one instrument company employs such an expression in their analytical software, allowing the investigator a wide choice in the analysis of experimental non-isothermal data.

MODEL CALCULATIONS

An existing Fortran program, KINMOD, developed to investigate simulated multiple reaction data under non-isothermal conditions [20] has been modified in order to compare form 1 and 2 analyses of single reactions. It also enables extent and rate of reaction data to be generated according to

TABLE 2

Summary of form 2 analyses on simulated form 1 data. Model parameters: $E = 220$ kJ mol^{-1}; $A = 1 \cdot 250 \times 10^{15}$ min^{-1}

Model	Z	$\alpha_{\max}$	$n_{\text{calc.}}$	Arrhenius		Kissinger		Friedman		
				$\bar{E}_A$ kJ mol^{-1}	$\bar{A}_A \times 10^{-15}$ min^{-1}	E_K kJ mol^{-1}	$A_K \times 10^{-15}$ min^{-1}	$\bar{E}_F$ kJ mol^{-1}	$\bar{A}_F \times 10^{-15}$ min^{-1}	k^*
A3 (A*n*)		0.628–0.623	4.11–2.28	220.0 ± 0.08	3.737 ± 0.047	220.1	3.810	219.5 ± 0.52	3.532 ± 0.291	2.7027
A2 (A*n*)		0.628–0.621	2.60–1.81	220.0 ± 0.01	2.501 ± 0.019	220.2	2.573	219.7 ± 0.50	2.429 ± 0.183	2.6894
R3 (R*n*)		0.688 ± 0.001	3.00 ± 0.02	220.0 ± 0.02	3.755 ± 0.018	220.0	3.761	219.8 ± 0.55	3.737 ± 0.343	2.1697
R2 (R*n*)		0.736 ± 0.001	2.00 ± 0.01	220.0 ± 0.02	2.501 ± 0.009	219.9	2.474	219.6 ± 0.58	2.426 ± 0.206	1.9470
D3		0.672 ± 0.002		220.0 ± 0.01	1.873 ± 0.002	220.2	1.920	219.6 ± 0.61	1.791 ± 0.201	0.6559
D4		0.751 ± 0.001		220.0 ± 0.01	1.872 ± 0.003	220.0	1.856	219.8 ± 0.77	1.855 ± 0.253	0.5897
D3 [a]				220.0 ± 0.007	1.249 ± 0.002	220.2	1.280	219.6 ± 0.61	1.194 ± 0.135	
D4 [b]				220.0 ± 0.002	1.248 ± 0.002	220.0	1.238	219.8 ± 0.77	1.236 ± 0.169	
C [a]	1.25	0.759 ± 0.001		225.5–223.2	3.431–1.908	219.6	0.918	219.6 ± 0.60	1.506 ± 0.603	
C [b]				222.3–221.4	1.679–1.325	219.9	1.064	219.6 ± 0.60	1.046 ± 0.136	
C [a]	1.50	0.766 ± 0.001		228.2–224.3	5.160–1.971	219.6	0.812	219.6 ± 0.67	1.356 ± 0.526	
C [b]				224.4–222.6	2.177–1.401	219.9	0.953	219.6 ± 0.67	0.943 ± 0.128	
C [a]	1.75	0.770 ± 0.001		230.3–225.3	6.883–2.096	219.5	0.732	219.6 ± 0.87	0.675–3.541	
C [b]				226.1–223.7	2.712–1.493	219.9	0.868	219.6 ± 0.87	0.880 ± 1.892	
C [a]	2.00	0.774 ± 0.001		231.9–226.2	8.753–2.185	219.6	0.679	219.8 ± 0.60	0.690–2.898	
C [b]				227.5–224.6	3.253–1.564	219.9	0.811	219.8 ± 0.60	0.842 ± 1.460	

[a] Analysed as form 1 D3.

[b] Analysed as form 1 D4.

the Carter [21] equation for three-dimensional diffusive rate-controlling reactions with varying molar volume ratios of product to reactant, Z, and subsequently analyzed according to the more simple form 1 models, D3 and D4.

Table 2 summarizes the findings of form 2 Arrhenius, Kissinger and Friedman analyses [20,22] on form 1 generated $\alpha - T$ and $\mathrm{d}\alpha/\mathrm{d}t - T$ data, assuming $E = 220$ kJ mol^{-1} and $A = 1.25 \times 10^{15}$ min^{-1}, under non-isothermal conditions, with a 100-fold change in linear heating rates, for the first four models listed in Table 1. The n values for the exponents in the An and Rn model calculations were evaluated from the measured $\alpha_{\max}$ values corresponding to $(\mathrm{d}\alpha/\mathrm{d}t)_{\max}$, as previously indicated [23]. The Friedman analyses covered the extent of reaction range $0.05 \leqslant \alpha \leqslant 0.95$. Data for the Carter three-dimensional diffusion model [21] was generated for various values of Z, between 1.25 and 2.0, and analyzed according to both the form 1 D3 and D4 models.

DISCUSSION

As regards the comparison of form 1 and form 2 expressions, the calculations confirm what is obvious from eqns. (1) and (2) and the $f(\alpha)$ expressions listed in Table 1, and which was previously indicated for the Avrami–Erofeev model by Fatemi et al. [4], namely

$$E_2 = E_1 \tag{7a}$$

$$A_2 = k^{\star} A_1 \tag{7b}$$

where $k^{\star}$ is the form 1 k_2 value. In attempting to decide which of the two forms, 1 or 2, should be adopted by the thermoanalytical community in order to standardize data analysis, Fatemi et al. [4] suggested a compromise, namely, $k^{\star}$ should be chosen such that, at $\alpha = 0.5$, $f(\alpha) = 1$. They have tabulated the appropriate $k^{\star}$ values for a number of solid state models. In the case of non-isothermal measurements, it is suggested that, if a compromise is to be made, a more suitable one is to define $k^{\star}$ such that $f(\alpha)[\alpha = \alpha_{\max}] = 1$. $\alpha_{\max}$ is essentially independent of heating rate for all models, and, as can easily be shown, takes the same value irrespective of the values used for the k_1 and k_2 multipliers in the $f(\alpha)$ and $g(\alpha)$ expressions. The appropriate values of $k^{\star}$ are given on the right hand side of Table 2. For the two-dimensional diffusion model, D2, $k^{\star} = 0.2084$, while for first and second order reactions $k^{\star}$ takes the values 1.634 and 4.470, respectively. The value of the correcting term, $-f'(\alpha_{\max})$ [23], used in the generalized Kissinger equation [22], will also be multiplied by $k^{\star}$. This has the effect of raising the low values for the nucleation and phase boundary movement models An (from 0.4 to 1.0) and Rn (from 1 to 2), while lowering the values for the diffusion models D3 (from 6.5 to 4.3) and D4 (from 6.1 to 3.6). Since the effect of the term in the Kissinger analysis is relatively small, the added affect of the $k^\star$ multiplier, as regards the calculated values of E_K and A_K, will be minor. It is considered that, since the effect of using the $k^\star$ multiplier compromise is so small, it will only add to confusion and, therefore, should not be employed. Furthermore, it is suggested that the use of form 1 expressions be universally adopted. They are, in the main, the forms used by most workers, and, furthermore, are as introduced by the various original investigators.

As is seen in Table 2, for the phase boundary movement and diffusion models, there is little variance in the α_{max} values over the wide heating rate range used in the simulation. However, such is not the case with the Avrami–Erofeev modeled data. Even though the relative variation in α_{max} is $< 0.3\%$, it results in a relatively wide range in the n values of the exponents in $f(\alpha)$ and $g(\alpha)$, namely: A3 ($n = 2.97 \pm 0.5$); A2 ($n = 2.16 \pm 0.3$). If such is the norm in analyzing experimentally error-free simulated data, it is not too surprising that wide variations are observed with experimental data [10,11,14].

Turning now to the three-dimensional diffusion situation, the relevant data for the simulated Jander ($D3$) and Gintsling–Brounshtein (D4) models with $E = 220$ kJ mol^{-1} and $A = 1.25 \times 10^{15}$ min^{-1}, using the form 1 expressions, are as shown in the lower half of Table 2. As is obvious from a consideration of the Carter integral expression, $g(\alpha)$, it is only applicable for $Z > 1$. As pointed out by Carter in his addendum, [21b] if one follows the same development [21a] of the $g(\alpha)$ function for the case $Z = 1$, one arrives at the Gintsling–Brownshtein expression [24]. Figure 1 shows (a) the complement of the extent, $(1 - \alpha)$, and (b) the rate, $(d\alpha/dt)$, of reaction at 10 °C min^{-1} for form 1 model D4 (curve 1), and the analogous four Carter models, with $Z = 1.25$, 1.50, 1.75 and 2.00 (curves 2–5). The peak parameters α_{max}, $\dot{\alpha}_{max}$ and T_{max} all increase linearly with increase in Z. This is true for all heating rates (β). Simulated data, generated over a 100-fold change in β, using the Carter expressions for $f(\alpha)$ and $g(\alpha)$, has been subjected to Arrhenius, Kissinger and Friedman analyses, employing both form 1 models, D3 and D4, with the results summarized in Table 2. As is seen, Arrhenius analyses yield a range of E_A and A_A values, the limiting values of which increase with increase in Z. The values obtained using the D3 model are larger than those resulting from use of the D4 model.

More consistent values were obtained from the Kissinger and Friedman analyses. As is seen, the mean values $\bar{E}_F$ and $\bar{A}_F$ are very close to E_K and A_K. The calculated activation energies are as selected for the simulation, namely, 220 kJ mol^{-1}. The A_K and A_F values decrease linearly with increase in Z. The correct value of the pre-exponential factor may be obtained from the value calculated, assuming the D4 coefficient for the $-f'(\alpha_{max})$ correction term [23] in the generalized Kissinger equation [22], by use of the

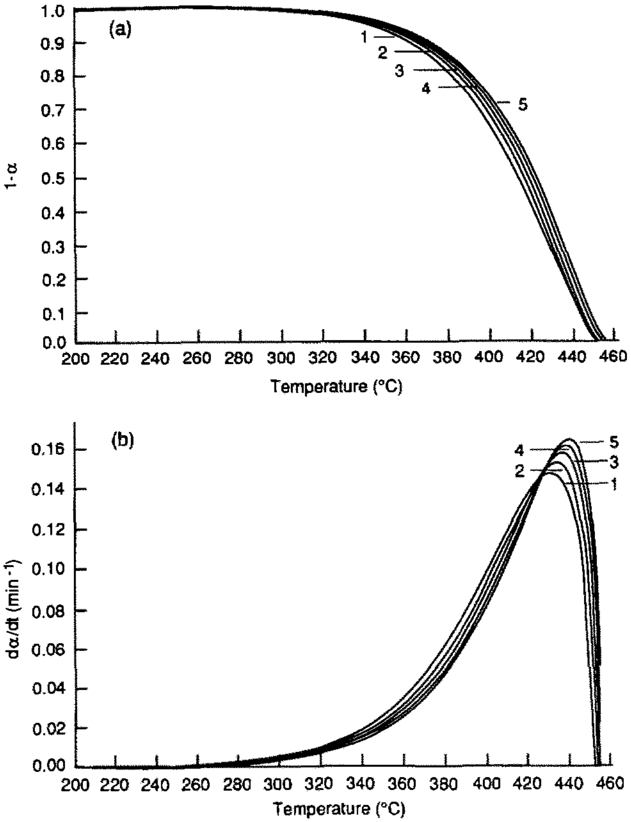

Fig. 1. Complement of the extent (a) and rate (b) of reaction as functions of temperature at 10 °C min^{-1}. Model D4, $Z=1.0$ (1), 1.25 (2), 1.50 (3), 1.74 (4) and 2.0 (5).

empirical relationship (8)

$$A_{\text{K}}(\text{correct}) = A_{\text{K}}(\text{calculated}) \times 100/(100 + k_3 - k_4 Z) \qquad (8)$$

Analogous simulations to those discussed so far have been performed, covering the range of values $E \approx 100$–440 kJ mol^{-1}, $A \approx 10^7$–10^{22} min^{-1}, and also, using $m = 1$ in the rate equation (2), $A \approx 10^4$–10^{19} K^{-1} min^{-1}. The resulting values of k_3 and k_4 are summarized in Table 3. Since only estimates are being made, it is considered sufficient to use the mean values,

TABLE 3

Model D4 Kissinger analysis. Pre-exponential factor Z adjustment coefficients

E/RT Range [a]	E_K	$m=0$		$m=1$	
		k_3	k_4	k_3	k_4
17–22	100	21.20	29.42	19.68	28.66
35–40	220	19.05	27.34	20.47	28.18
52–57	440	18.25	27.39	18.52	26.98

[a] $\beta = 1$–100 °C min^{-1}.

$k_3 = 19.5$ and $k_4 = 28$, in all estimations. Thus, for example, for the thermal degradation of calcium carbonate ($Z = 2.2$) under a flowing nitrogen atmosphere [25], $E_K = 172.4$ kJ mol^{-1} and $A_K = 1.97 \times 10^4$ K^{-1} min^{-1}. The corrected value of A_K is thus 3.4×10^4 K^{-1} min^{-1}.

In summary, the form of the mathematical expressions employed for the functions $f(\alpha)$ and $g(\alpha)$ for the A2, A3, R2, R3, D3 and D4 solid state models only affects the value of the calculated pre-exponential factor, A, in the rate equation. Similarly, the use of the D4 model in analyzing data for reactions where the molar volumes of reactant and product differ also only affects the value of the pre-exponential factor. In all cases, the correct value of A may be obtained by use of the appropriate multiplicative constant.

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