

MULTIPLE REACTION SCHEME MODELLING*

IV. Mutually independent random nucleation reactions

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An analysis has been performed of the characteristics of the effective reactions, generated under non-isothermal conditions at constant heating rates, resulting from various equal weight combinations of sets of mutually independent, individual reactions obeying the Avrami-Erofeev kinetics laws in which two and three dimensional random nucleation phenomena are the rate-controlling mechanisms. As in previous analyses, dealing with multiple sets of first and n^{th} order singular reactions, with regard to the separation of the individual extent and rate of reaction - temperature curves, three model classes have been considered. The relative spacing at one defined temperature either decreases/increases by a set increment or remains constant. Sets comprising from five to fifty members have been examined.

The effective reaction data at each heating rate has been subjected to Arrhenius analysis, and data, generated over a range of heating rates, has been analyzed using the generalized Kissinger and Friedman iso-conversional approach. The effective reaction may be analyzed assuming it obeys the Avrami-Erofeev law or as an n^{th} order reaction. The several features resulting from the various analyses will be discussed.

In solid state thermophysical and thermochemical reactions, it is highly probable that the occurrence of multiple processes is more the rule than the exception. In such cases, it is the extent and rate of the effective reaction which is measured by, for example, thermoanalytical means. How useful then is such data? Further questions must be posed before this can be answered. Are there any patterns in the variation of calculated reaction kinetics parameters with the extent of the overall reaction? Which thermoanalytical approach is most useful, isothermal or non-isothermal?

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Are there any criteria by which to test for the occurrence of multiple reactions? What model reactions should be employed to attempt to establish such criteria?

In extending the work of Ozawa [1] and Flynn [2] the author [3] first concerned himself with studying simple models, namely, sets of mutually independent, first order reactions with close-valued reaction kinetics parameter E , A values. Realizing the limitations of the early work, a more rational approach to the construction of the model has been presented [4]. This analysis enabled the development of the first criterion of the occurrence of multiple reactions, namely, a characteristic variation in the Friedman [5] reaction kinetics parameters with extent of reaction. Such analyses necessitate the non-isothermal approach. A further result of this analysis is that a set of first order reactions yield an overall n^{th} order reaction, where the order can vary from 0.6 to 3.0.

More recently, this multiple reaction scheme analysis has been extended to cover multiple sets of the n^{th} order reactions [6]. This treatment confirmed the first criterion, and enabled the development of a second. Two equations relating the maximum rate parameters, the Arrhenius activation energy, the order of reaction and the heating rate may be generated from the rate equation and its integral form, (Eqs 3 and 5) [6]. The first is generally applicable, but the second is valid strictly for a single reaction. A difference between the n -values, calculated by these two means, is indicative of a multiple reaction. Furthermore, the magnitude and sign of the difference is characteristic of the complexity of the multiple set model.

Solid state reactions of great interest are those that involve nucleation or associated phenomena. The random nature of such nucleation phenomena may well generate a multiple reaction situation, which should be examined. Šestak [7a] has discussed the several solid state processes belonging to the general class. It should be pointed out that there are differences in the published integral form, $F(\alpha) = h \cdot [-\ln(1 - \alpha)]^{1/n'}$, of the $f(\alpha)$ function describing these processes, where n' is the Avrami exponent. Thus, Sharp, Brindley and Achar [8], in generating numerical data applicable to the first discussed members of this class, the Avrami-Erofeev growth processes by two and three dimensional random nucleation (A2, A3), set $h = 1$, which is correct. The differential form, used in the rate equation, *vide infra*, then becomes $f(\alpha) = n' \cdot (1 - \alpha) \cdot [-\ln(1 - \alpha)]^{(n'-1)/n'}$. Heal, quoted by Brown, Dollimore and Galwey [9], uses $h = n'$. In this case, $f(\alpha) = (1 - \alpha) \cdot [-\ln(1 - \alpha)]^{(n'-1)/n'}$. Šestak [7b], employing the symbol G for this class, uses this latter form $f(\alpha)$, but tabulates the integral function with $h = 1/n'$. Calculations have shown

that the results presented in this analysis are essentially the same, irrespective of the value of h . Here, the Heal relationships have been employed, since presumably they are the most widely accepted mathematical forms.

In this paper, an analysis is made of the characteristic features of the effective reaction resulting from sets of individual Avrami-Erofeev, A2/A3 reactions, assumed to proceed in a mutually independent fashion. As in previous work, [3, 4, 6] three classes of multiple sets will be generated. These classes enable different possible arrangements of the single member extent and rate of reaction curves on the temperature axis. Multiple sets comprising from five to fifty individual members will be considered. The effective reaction data, generated over a wide range of linear heating rates will be subjected to Arrhenius, Friedman and Kissinger analyses.

Theoretical basis

The effective reaction resulting from a mutually independent combination of the individual member reactions of a multiple set is given by equations (1) - (4).

$$\frac{d\alpha}{dt} = \sum g_i \frac{d\alpha_i}{dt} \quad (1)$$

$$F(\alpha) = \sum g_i F(\alpha_i) \quad (2)$$

$$F(\alpha_i) = \int_0^{\alpha_i} \frac{d\alpha}{f(\alpha_i)} \quad (3)$$

$$\sum g_i = 1 \quad (4)$$

In this analysis, for simplicity, the L individual reactions are assumed to contribute equally to the overall reaction, i.e., $g_i = 1/L$. Each singular reaction is assumed to follow the solid state reaction rate law, equation (5), with $f(\alpha_i)$ given by (6) where $n' = 2$ or 3 .

$$d\alpha_i / dt = A \cdot T \cdot \exp(-E / RT) \cdot f(\alpha_i) \quad (5)$$

$$f(\alpha_i) = (1 - \alpha_i) \cdot [-\ln(1 - \alpha_i)]^{(n'-1)/n'} \quad (6)$$

The effective reaction may be analyzed in either of two ways: (a) it is as-

sumed to follow the same law as the individual reactions from which it is constructed, (b) as an n^{th} order reaction. The $f(\alpha)$ function takes either of the forms 6a or 6b.

$$An' \text{ models } (n' = 2, 3) \quad f(\alpha) = (1 - \alpha) \cdot [-\ln(1 - \alpha)]^{(n'-1)/n'} \quad (6a)$$

$$Fn \text{ model} \quad f(\alpha) = (1 - \alpha)^n \quad (6b)$$

The extent of reaction at the maximum rate is given by either (7a) or (7b).

$$An' \text{ models } (n' = 2, 3) \quad \alpha_{\max} = 1 - \exp(1 - n' - \eta) / n' \quad (7a)$$

$$Fn \text{ model} \quad \alpha_{\max} = 1 - [1 - \eta \cdot (n - 1) / n]^{1/(n-1)} \quad (7b)$$

The extents of reaction at the selected heating rate, β , are calculated from $F(\alpha)$, which, as has been shown [10] is given by the general expression (8).

$$F(\alpha) = (A / \beta) \cdot (E / R)^2 \cdot p_1(E / RT) \quad (8)$$

For the two analyses:

$$An' \text{ models } (n' = 2, 3) \quad F(\alpha) = n' \cdot [-\ln(1 - \alpha)]^{1/n'} \quad (9a)$$

$$Fn \text{ model} \quad F(\alpha) = [1 - (1 - \alpha)^{1-n}] / (1 - n) \quad (9b)$$

The η and p_1 functions, in equations (7) and (8) respectively, are given by equations (10) and (11), where $x = E / RT$

$$\eta = [1 + 1/x] \cdot p_1(x) \cdot x^3 \cdot e^x \quad (10)$$

$$p_1(x) = \int_{T_0}^T T \cdot \exp(x) dT \quad (11)$$

As previously indicated [10] a generalized Doyle equation is employed to evaluate $p_1(x)$. With $x \geq 30$, the relative deviation from the exact Vallet [11] values is < 0.001 .

Non-isothermal extent and rate of reaction data so generated at several linear heating rates, β , is analyzed by the Friedman iso-conversion equation (12).

$$\ln[(d\alpha / dt)_\alpha / T_\alpha \cdot f(\alpha)] = \ln A_F - E_F / RT_\alpha \quad (12)$$

and the generalized Kissinger equation (13).

$$\ln(\beta / T_{\max}^3) = \ln(A_K \cdot E_K / R) + \ln \theta_1(\alpha_{\max}) \cdot E_K / RT_{\max} \quad (13)$$

$$\text{where } \theta_1(\alpha_{\max}) = -f(\alpha_{\max}) / (1 + RT_{\max} / E_K) \quad (14)$$

The $-f(\alpha_{\max})$ function is given by either (15a) or (15b).

$$An' \text{ models } (n' = 2, 3) \quad -f(\alpha_{\max}) = [n' \eta^{n'} / (n' + \eta - 1)]^{1/n'} \quad (15a)$$

$$Fn \text{ model} \quad -f(\alpha_{\max}) = n - (n - 1) \cdot \eta \quad (15b)$$

Following the procedure previously described [4] three classes of multiple sets will be considered. They are defined in terms of their reaction kinetics parameters, generated by program PARCAL. The extent (α) and rate ($\dot{\alpha}$) of reaction - temperature data of the initial member of the set, the master curves are generated at a set heating rate over the range $\alpha = 0.001$ to 0.999, and $\alpha_1(\max)$, $\dot{\alpha}_1(\max)$ and $T_1(\max)$ defined. These master curves are displaced along the temperature axis by an increment ΔT_i . The E_i , A_i values of each displaced curve are obtained by Arrhenius analysis, (equation 5). ΔT_i is evaluated at $T_1(\max)$ such that, at this temperature, the relative spacing between contiguous curves either remains constant, increases or decreases by a set fraction. A simple alphanumeric code is used to identify a multiple set. For example, 5I, 20D and E, refer to sets in which the relative spacing increases by 5%, decreases by 20% or remains equal, respectively. The actual spacing depends, of course on the selected relative positions of the first and last member $\alpha - T$, $\dot{\alpha} - T$ curves. These are defined by the ratio $f = \alpha_L / \alpha_1$ at $T_1(\max)$, selected by the investigator. Using the E_i , A_i values for each singular reaction in the multiple set, program KINMOD [3] generates the extent and rate of reaction- temperature data of the normalized effective reaction over the range $\alpha_{\text{eff}} = 0.001$ to 0.999 at a chosen heating rate. An Arrhenius analysis is then performed assuming either the single reaction model (A2/A3), a generalized An' model or an Fn model. This procedure is repeated for a range of heating rates, $\beta = 1 - 150$ deg/min. The program concludes with a generalized Kissinger analysis, and a Friedman analysis for $\alpha_{\text{eff}} = 0.05 - 0.95$ at 0.05 intervals, assuming in turn the three models, A2/A3, An and Fn .

Analytical results

As in previous work, [3, 4, 6] the values $E_1 = 220$ kJ/mol and $A_1 = 1.250 \cdot 10^{12} \text{ K}^{-1} \cdot \text{min}^{-1}$ are used throughout the analysis for the master reaction. Before examining multiple sets, it is important first to consider the master reaction.

Figures 1a and 1b show the complement of the extent ($1 - \alpha$) and the rate ($d\alpha/dt$) of reaction, respectively, as functions of temperature for $f(\alpha)$, given by equation 6a, for various values of n' , at 10 deg/min. Although the maximum reaction rate decreases linearly with decrease in n' , both α_{\max} and T_{\max} decrease to a much lesser extent, and in a non-linear manner. It is easily shown that a $\pm 0.5\%$ error in α_{\max} results in a $+86\%$, -32% error in n' . A $\pm 0.5\%$ error in T_{\max} results in a $\pm 8\%$ error in n' . To emphasize this fur-

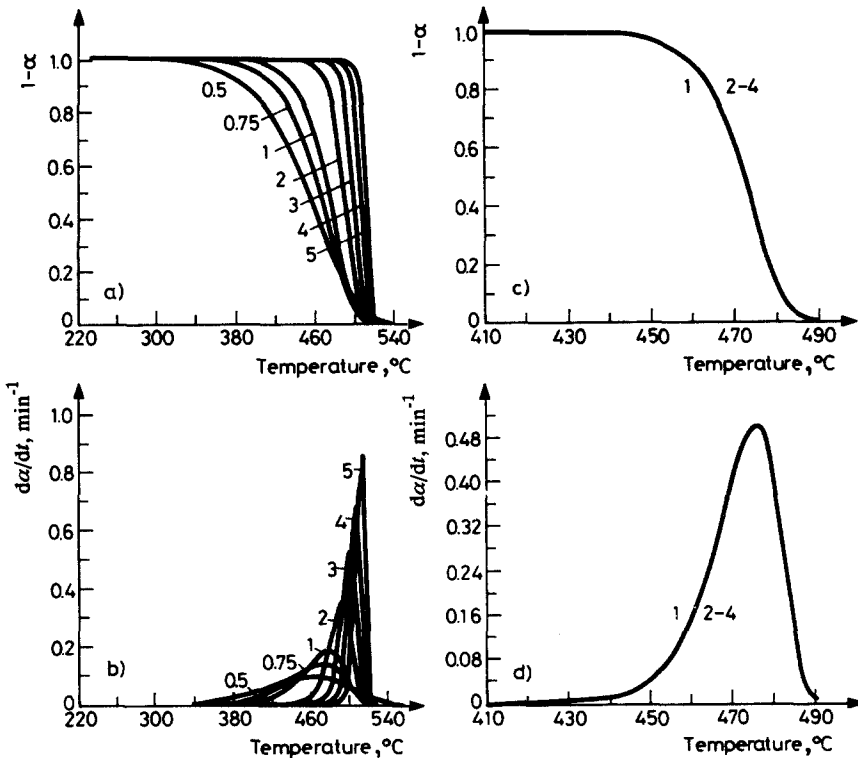


Fig. 1 An' master reactions, complement of extent and rate of reaction vs. temperature at 10 deg/min. (a), (b) $E = 220$ kJ/mol, $A = 1.25 \cdot 10^{12} (\text{K}^{-1} \cdot \text{min}^{-1})$. Various Avrami exponents. (c), (d) Table 2 reactions

ther, models A2 and A3 master reaction extent and rate of reaction - temperature data was generated at various heating rates in the range, 1-150 deg/min. Table 1 summarizes the results of the Kissinger and Friedman analyses. For model A2, the energies of activation and pre-exponential factor values are consistent, even though the $\pm 0.18\%$ variation in α_{\max} results in a $\pm 11\%$ spread in the value of n' , calculated from equation 7a. However, for model A3, the $\pm 0.26\%$ variation in α_{\max} results in an n' -value of 3.27 with a $\pm 23\%$ spread. This, in turn, affects both the Kissinger and Friedman analytical data, as indicated. For both A2 and A3 model data, when analyzed as an n^{th} order reaction, although the correct energies of activation are obtained, the A_K -values are low, and the A_F -values exhibit a slight increase over the range, $\alpha = 0.05 - 0.95$.

Great care has to be exercised when extent and rate of reaction data, either experimental or simulated, as in this analysis, is subjected to reaction kinetics analysis using the Avrami-Erofeev models. To emphasize this further, consider the four widely disparate model An' reactions, #1-4, listed in Table 2. The $1 - \alpha$ vs. T , and $d\alpha/dt$ vs. T curves, generated at 10 deg/min, are shown in Fig. 1c and 1d, respectively. With the exception of reaction #1 in the region $\alpha = 0.05$ to 0.25 , the curves are essentially the same, as confirmed by the α_{\max} , $\dot{\alpha}_{\max}$ and T_{\max} values given in Table 2. Thus, equality of the maximum reaction rate parameters does not necessarily imply equality of model An' E_A , A_A , n' values. However, when each of the four separate sets of extent and rate of reaction data was subjected to Arrhenius analysis, assuming an n^{th} order reaction, consistent E_A , A_A , n values were obtained, as shown in Table 2. The small difference in the $1 - \alpha$, $d\alpha/dt - T$ data for reaction #1 compared with reactions #2-4 shows up in the slightly lower model Fn reaction kinetics parameter values. The consistency of this model Fn data is in contrast to the statements and conclusions of Arnold *at al* [12] in their discussion of n^{th} order reactions.

Multiple set analysis

Table 3 lists the important parameters of a PARCAL output for a 5-member, model A2 set, with 5I spacing and $\alpha_5/\alpha_1 = f = 0.05$. It is seen that the change in the ratio α_i/α_1 for each contiguous member reaction indeed increases by 5%. In order to study the effect of different spacing between contiguous curves, one generally employs as wide a window (smallest f) as possible, such that the effective reaction shows a single maximum rate. The

Table 1 Variability of reaction kinetics parameters for model An' master reactions

	Model An'	Model $F'n$	Model An'
α_1 (max)	0.6222 \pm 0.0011		
n' (n)	2.009 \pm 0.224	0.949 \pm 0.006	2
E_K , kJ/mol	220.5	219.9	220.0
$A_K \cdot 10^{-12}$, (K.min) ⁻¹	1.350	0.588	1.253
E_F , kJ/mol	219.8 \pm 0.6	219.5 \pm 0.6	219.7 \pm 0.6
$A_F \cdot 10^{-12}$, (K.min) ⁻¹	1.238 \pm 0.116	0.250 - 1.697	1.223 \pm 0.124
α_1 (max)	0.6258 \pm 0.0016		
n' (n)	3.265 \pm 0.735	0.931 \pm 0.007	3
E_K , kJ/mol	211.0	219.8	220.0
$A_K \cdot 10^{-12}$, (K.min) ⁻¹	0.322	0.389	1.258
E_F , kJ/mol	212.9 - 221.4	219.7 \pm 0.6	219.7 \pm 0.6
$A_F \cdot 10^{-12}$, (K.min) ⁻¹	0.436 - 1.849	0.190 - 1.987	1.223 \pm 0.104

Table 2. Various model An' reaction kinetics parameters

Model	Reaction	n' (n)	E_A kJ/mol	A_A (K.min) ⁻¹	α_{max}	$\dot{\alpha}_{max}$	T_{max} °C
An'	1	5.22	101.3	$2.156 \cdot 10^4$	0.6279	0.5007	475.0
	2	2.90	200.2	$1.717 \cdot 10^{11}$	0.6262	0.5002	475.0
	3	1.99	300.0	$1.585 \cdot 10^{18}$	0.6230	0.5008	475.0
	4	1.52	399.6	$1.413 \cdot 10^{25}$	0.6249	0.5008	475.0
Fn	1	0.98	595.4	$6.518 \cdot 10^{38}$			
	2	0.99	612.5	$1.017 \cdot 10^{40}$			
	3	1.01	616.9	$2.120 \cdot 10^{40}$			
	4	1.00	614.8	$1.492 \cdot 10^{40}$			

limiting value of f is dependent both upon the selected type of curve spacing, and the number of members in the set. Table 4 lists the singular E_i, A_i values of the member reactions of three multiple sets with different modes of α_i vs. T curve spacing, calculated at 10 deg/min. The $1 - \alpha_i$ and $d\alpha_i/dt$ curves, together with those for the effective reactions, (dotted curves) are shown in Fig. 2. The displacement of the individual curves along the temperature axis is given by $T_i(\max) - T_1(\max)$. The α_{\max} and T_{\max} values for the normalized effective reactions are as indicated in Table 4. Assuming that the overall reactions obey the same kinetics law as the individual member reactions, Arrhenius analysis yields the indicated E_A, A_A values. Using these with the α_{\max} and T_{\max} values, an effective Avrami exponent may be calculated from equation 7a.

Table 3 Typical multiple set data - PARCAL output 5-member set, 5I spacing, $f = 0.05$, 10 deg/min

i	E_i kJ/mol	$A_i \cdot 10^{-12}$ (K.min) ⁻¹	α_i	ΔT^*	α_i / α_1 %	$\Delta \alpha_i / \alpha_1$ %
1	220.0	1.250	0.62505	-	100.00	-
2	222.3	1.484	0.48728	3.91	77.96	22.04
3	225.2	1.874	0.34263	8.60	54.82	23.14
4	229.6	2.170	0.19074	15.38	30.52	24.30
5	240.8	6.357	0.03125	33.61	5.00	25.52

*At $T_1(\max)$

Extremely low values, ~ 0.2 , are obtained, which in turn yield absurdly high E_A, A_A values. If, however, the effective reactions are analyzed assuming an n^{th} order law, equations 6b and 7b, more realistic E_A, A_A values result, as shown in Table 4. All these tabulated reaction kinetics parameters were obtained using the entire $\alpha - T$ and $\dot{\alpha} - T$ data of the effective reactions, with a realistic limit to the allowable deviation from linearity in performing the Arrhenius analysis, (see Elder [4] for details), namely 5, 10 and 15% for the three models, respectively. The agreement between the actual $\alpha - T$ curves for the effective reaction and those calculated using the n^{th} order parameters for the 10-member and 5-member model A2 multiple sets is excellent. Even in the α_{\max} region, the difference $\Delta\alpha < 0.01$. Unfortunately, the dynamic range of the computer used in this analysis, is such that the $\alpha - T$ values in the n^{th} order analysis of the 10-member model A3 multiple set effective reaction, which, as indicated in Table 4, has exceedingly high E, A values, cannot be calculated. As has been pointed out previously [4, 6], Friedman analysis, i.e. iso-conversional Arrhenius analysis, is the preferred

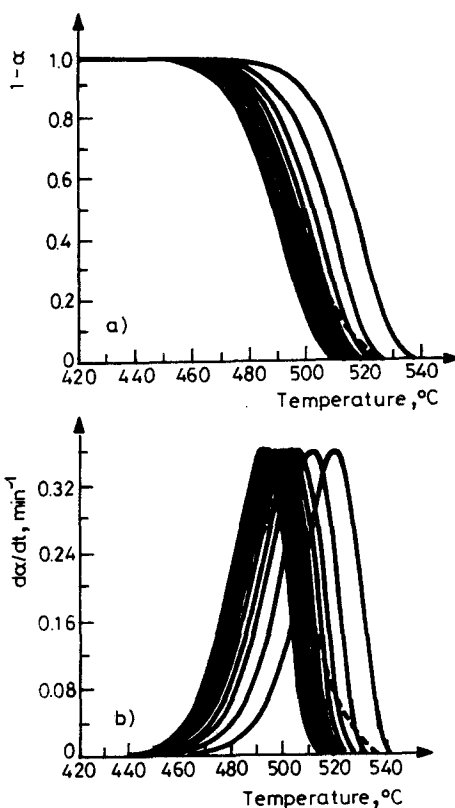


Fig. 2a, b Complement of extent and rate of reaction vs. temperature at 10 deg/min.
(a), (b) 10-member A2 set, 10I spacing, $\alpha_{10}/\alpha_1 = 0.1$

thermoanalytical tool, and fortunately, yields E_F , A_F values such that the necessary $\alpha - T$ calculations lie within the computer's dynamic range

If the width of the $\alpha - T$ window is limited by setting $f = \alpha_L / \alpha_1 = 0.7$, and limiting the number of members to $L \leq 10$, multiple sets may be generated such that the effective reaction can be analyzed assuming the An' model, yielding apparently realistic values for the reaction kinetics parameters. Fig. 3a shows the $1 - \alpha_i$ vs. T curves, and the effective reaction (dotted curve) at 10 deg/min. for such a narrow window, 5-member set of model A2 reactions with fixed E_i values: $E_1 = 220$, $\Delta E = 0.8$ kJ/mol, $\ln A_i = 0.07843.E_i + 10.60$. The curves are $7.5E$ spaced at $T_1(\max) = 493.2^\circ$. As is seen, the effective reaction is almost coincident with the third member, $E_3 = 221.6$ kJ/mol, $A_3 = 1.418.10^{12} \text{K}^{-1} \cdot \text{min}^{-1}$, $T_3(\max) = 495.8^\circ$. When analyzed as-

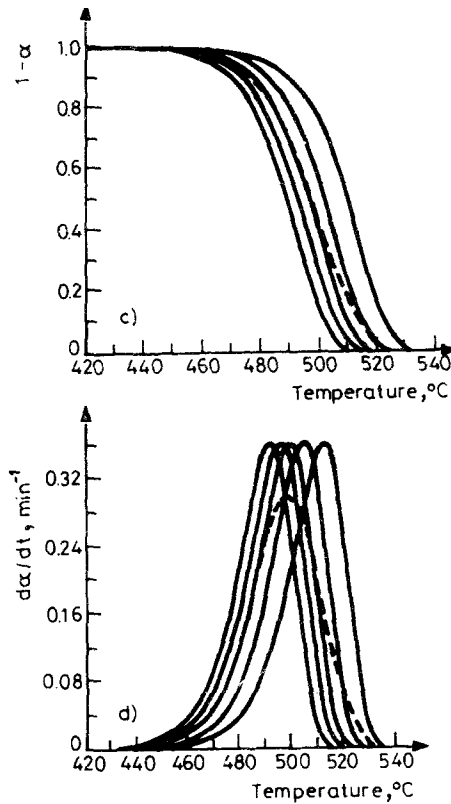


Fig. 2c, d Complement of extent and rate of reaction vs. temperature at 10 deg/min. ; (c), (d) 5-member A2 set, E spacing, $\alpha_5/\alpha_1 = 0.2$

suming model A2, the effective reaction yields $E_A = 217.8$ kJ/mol, $A_A = 0.758 \cdot 10^{12} \text{ K}^{-1}$, $T(\text{max}) = 495.6^{\circ}$. When analyzed as an An' reaction, one obtains $n' = 1.18$, $E_A = 385$ kJ/mol, $A_A = 1.701 \cdot 10^{23} \text{ K}^{-1} \cdot \text{min}^{-1}$. The magnitude of these variations are in accordance with those previously discussed (see Fig. 1c, Table 2).

If the window is broadened to $f = 0.25$, one obtains the curves with 18.75E spacing, shown in Fig. 3b, with $E_1 = 220$, $\Delta E = 2.7$ kJ/mol, $\ln A_i = 0.08125 \cdot E_i + 10.02$. The effective reaction, dotted curve, exhibits one maximum rate. However, although this reaction data can be analyzed according to the A2 model; $E_A = 215.6$ kJ/mol, $A_A = 0.426 \cdot 10^{12} \text{ K}^{-1} \cdot \text{min}^{-1}$, a meaningful model An' Arrhenius analysis cannot be performed. Finally, if $f = 0.05$, the relatively broad window, shown in Fig. 3c, with 23.75E curve spacing at 493.2° , $E_1 = 220$, $\Delta E = 5.2$ kJ/mol, $\ln A_i = 0.0838 \cdot E_i + 9.68$ results.

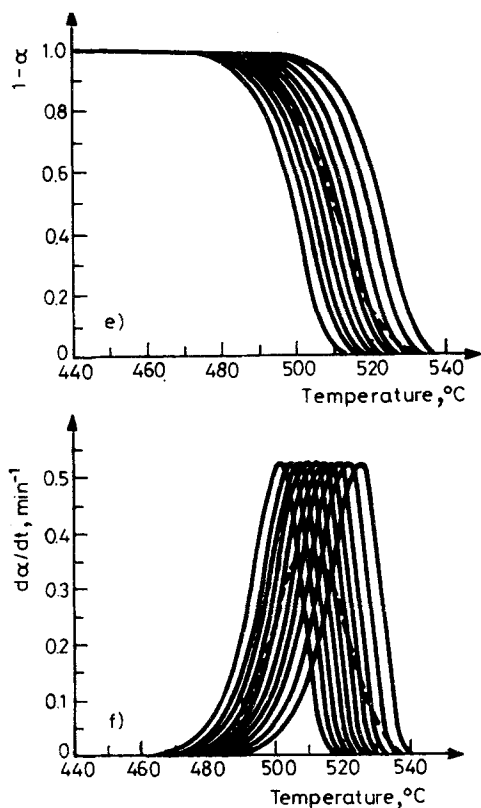


Fig. 2e, f Complement of extent and rate of reaction vs. temperature at 10 deg/min. (e), (f) 10-member A3 set, 20D spacing, $\alpha_{10}/\alpha_1 = 0.05$

The effective reaction rate shows a peak at $\alpha_{\max} = 0.4848$ at 499.5° with a slight shoulder at $\alpha \sim 0.98$ ~at 530° . Again, the effective reaction cannot be treated as a model An' reaction. Furthermore, only the data in the α - range 0.0 to 0.4454 can be used in a model A2 evaluation.

It is obvious that the effective reaction resulting from a set of either A2 or A3 individual reactions can, in general, only be analyzed assuming the n^{th} order model, equations 6b, 7b and 9b. For certain multiple sets, reaction kinetics evaluations, assuming the single reaction model, can be carried out. When evaluated as F_n reactions, the values of n are dependent upon the number of members in the set, and the type and magnitude of the relative spacing between contiguous $1 - \alpha_i$ vs. T curves. Figure 4 shows the curves of the extreme member single reactions and the effective reactions for the 5D

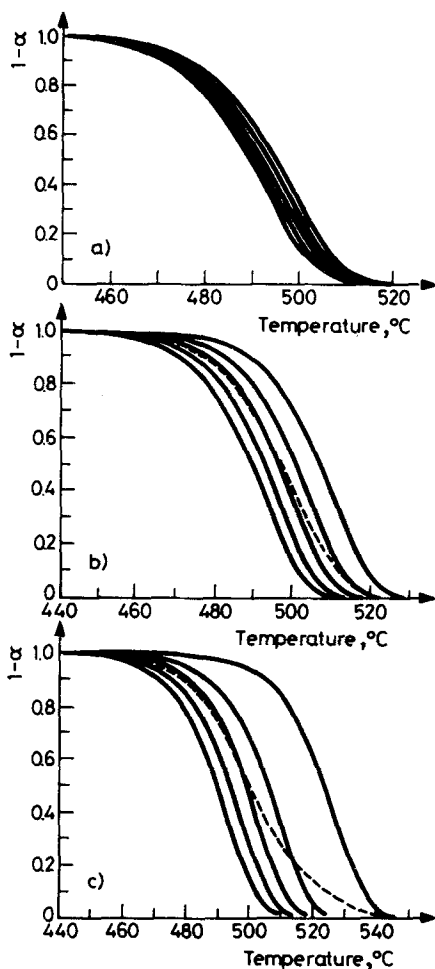


Fig. 3 Complement of extent of reaction vs. temperature at 10 deg/min. 5-member A2 set with E spacing with fixed ΔE values. (a) $\alpha_5 / \alpha_1 = 0.7$ $\Delta E = 0.8$ kJ/mol; (b) $\alpha_5 / \alpha_1 = 0.25$ $\Delta E = 2.7$ kJ/mol; (c) $\alpha_5 / \alpha_1 = 0.05$ $\Delta E = 5.2$ kJ/mol

and 20D, $f = 0.05$, 25-member, model A3 set, at 10 deg/min. The points X and Y indicate the maximum effective reaction rates, from which the n -values, 1.58 and 0.94 respectively, are calculated. In all cases, n is directly proportional to the logarithm of the heating rate, as shown in Fig. 5 (model A2) and Fig. 6 (model A3) for (a) 5, (b) 10, (c) 25 and (d) 50-member sets. The circles on the 30D lines in Figs 5a and 6a attest to the linearity of the data, which applies also in the other cases considered. As can be seen for

the 5-member sets, the slopes decrease as the relative spacing changes from 30D to 30I. For sets with D spacing, a reversal in the $n - \ln \beta$ slope can occur. The greater the number of members in the set, the lower the value of the D spacing at which the reversal occurs. Thus, for a 10-member set, between 20D and 30D; for a 25-member set, reversal occurs between 10D and 20D, and between 5D and 10D for a 50-member set. The $n - \ln \beta$ variation thus serves as an identifier of the multiple set. For models in which the change in relative spacing between contiguous $1 - \alpha_i$ vs. T curves is high, $\geq 10\%$, then as the number of members in the set increases, $L \geq 25$, so the

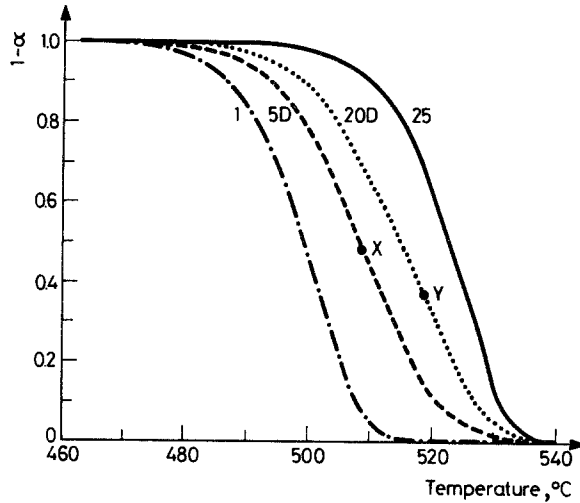


Fig. 4 Complement of extent of reaction vs. temperature at 10 deg/min. 25-member A3 set, extreme members 1 and 25, $\alpha_{25}/\alpha_1 = 0.05$. Effective reaction curves: 5D and 20D spacing

curves diverge or converge to such an extent that they are too close to differentiate either at the beginning (incremental spacing) or the end (decremental spacing). Such models are indicated in Figs 5 and 6 by their absence.

Friedman analyses of the effective extent and rate of reaction data for these several multiple sets, calculated over the linear heating rate range, 1 - 150 deg/min, have been carried out over the α - range, 0.05 to 0.95 at 0.05 intervals. The iso-conversional reaction kinetics parameters were calculated (a) assuming the effective reaction obeyed the same law as the individual reactions (A2 or A3) comprising the set, (b) as an n^{th} order (F_n) reaction. Since calculations have shown that, irrespective of the model employed, the

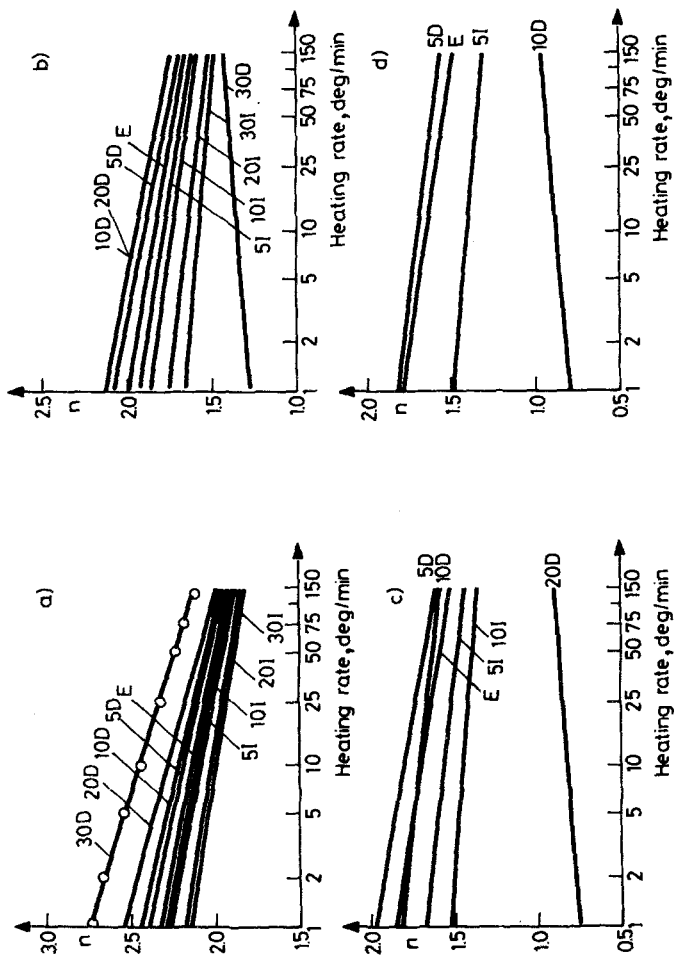


Fig. 5 Model A2 multiple sets. Effective reaction n^{th} order analysis n vs. β (semi-logarithmic plot). Various extent of reaction vs. temperature curve spacing. (a) 5 members (b) 10 members (c) 25 members (d) 50 members

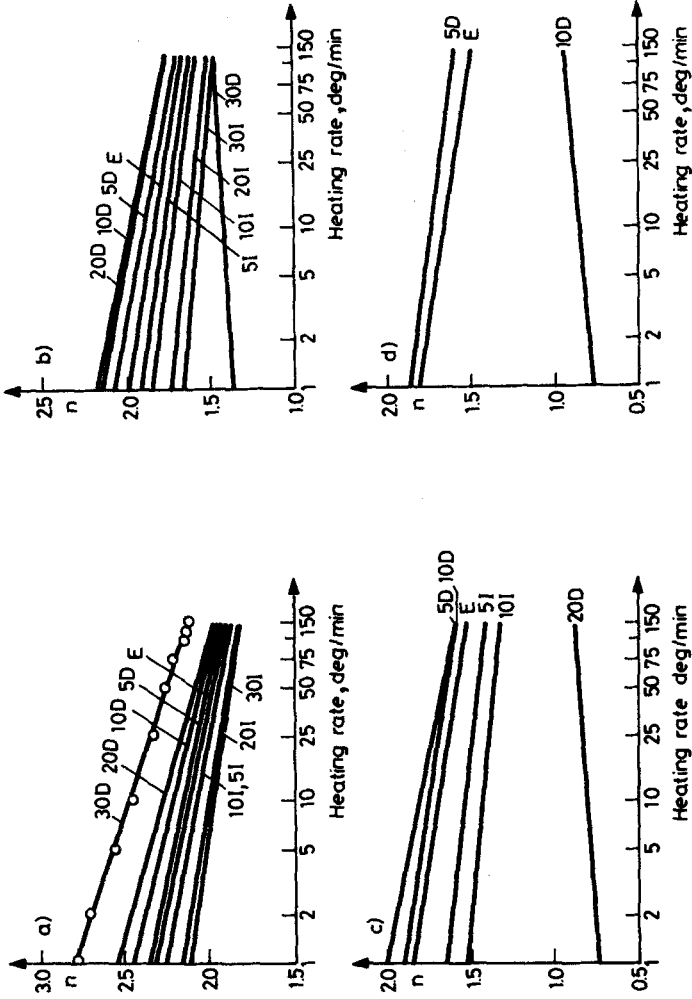


Fig. 6 Model A3 multiple sets. Effective reaction n^{th} order analysis n vs. β (semi-logarithmic plot). Various extent of reaction vs. temperature curve spacing. (a) 5 members (b) 10 members (c) 25 members (d) 50 members

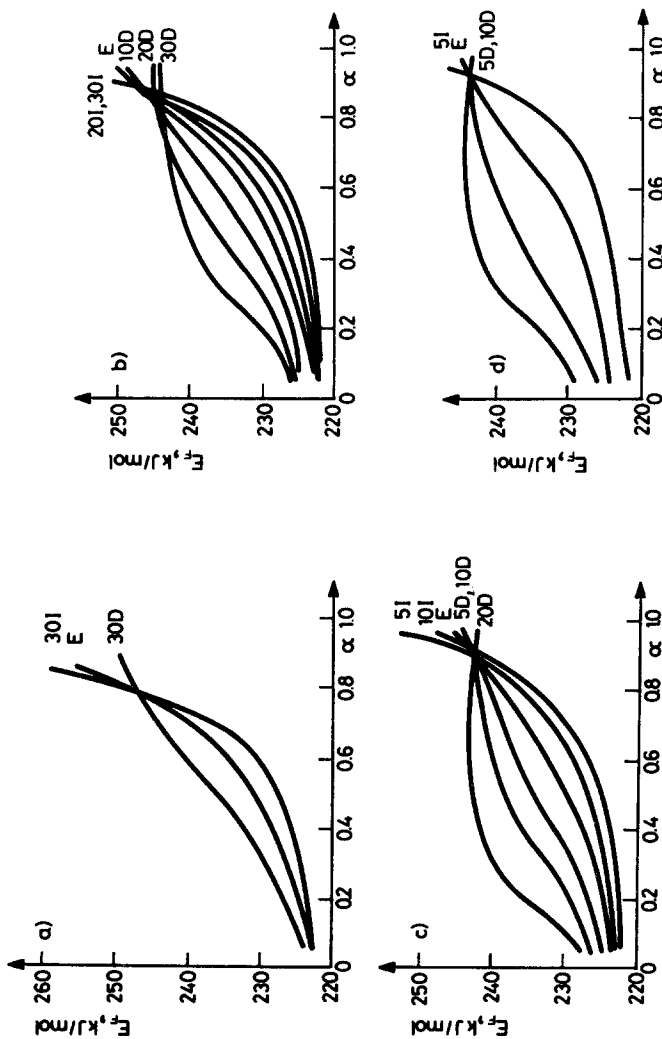


Fig. 7 E_F vs. α model A2 sets/A2 analyses. Various extent of reaction vs. temperature curve spacing. (a) 5 members (b) 10 members (c) 25 members (d) 50 members

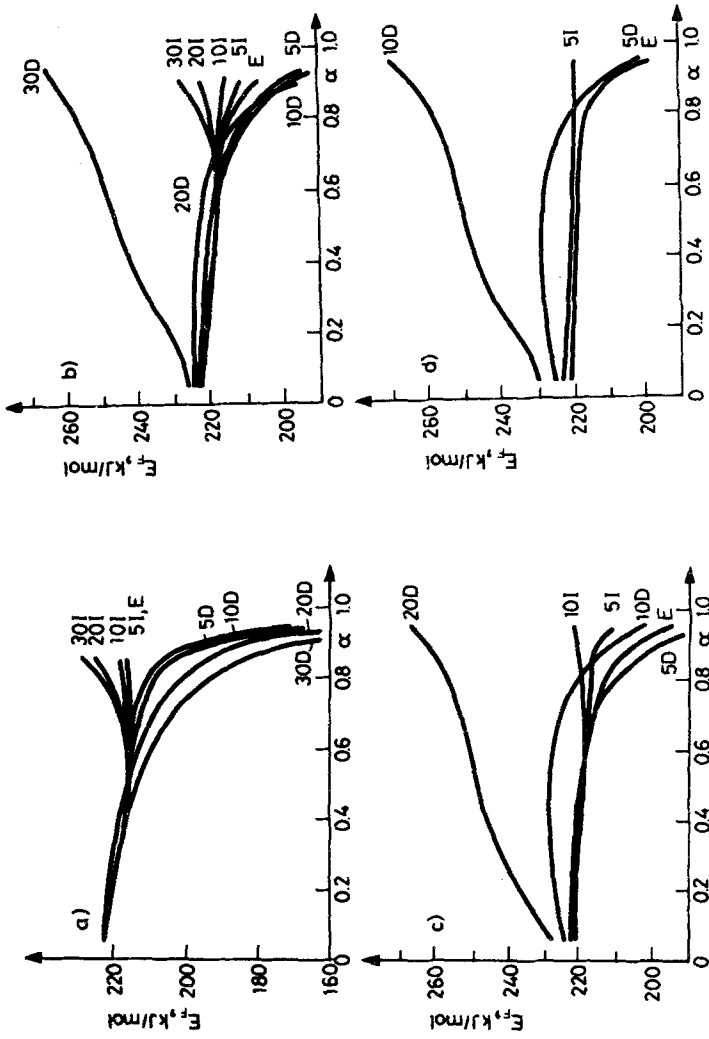


Fig. 8 E_F vs. α model A2 sets/ F_n analyses. Various extent of reaction vs. temperature curve spacing. (a) 5 members (b) 10 members (c) 25 members (d) 50 members

Friedman parameters obey the compensation relationship, equation (16), only the activation energy data will be presented.

$$\ln A_F = k_1 E_F + k_2 \quad (16)$$

For the model A2 individual reaction system, Figs 7 and 8 show the variation of E_F with the extent (α) of the effective reaction, evaluated as model A2 and F_n reactions, respectively, for (a) 5, (b) 10, (c) 25 and (d) 50 member sets. Figures 9 and 10 show the analogous plots for the A3 individual reactions system. There are very significant differences between the characteristic $E_F - \alpha$ variations according to the assumed effective reaction model. As can be seen from Figs 7 and 9, when analyzed as A2 and A3 reactions, the variations exhibit similar patterns as the individual member 1 - α_i vs. T curve spacing changes from high D through E to high I . When analyzed as F_n models, as shown in Figs 8 and 10, E_F shows a reasonably linear variation with α over $\sim 75 - 80\%$ of the total reaction. It is only in the final 20-25% of the effective reaction that the larger variations, particularly so in the case of the 5D-30D models, are encountered. As is also seen, for the E and 5I-30I models, the change in E_F with α is small. The exceptions for the 10-member-30D, 25 member-20D and 50 member-10D models in Figs 8b-8d, 10b-10d, parallel those indicated in Figs 5b-5d, 6b-6d. The compensation coefficients in equation 16 are given for the A2/A3 and F_n evaluations in Tables 5 and 6, respectively. For the model A2 and A3 evaluations, as can be seen from Table 5, k_1 and k_2 remain relatively constant, independent of the number of members in the multiple set, and the model type. For the F_n evaluations, as shown in Table 6, k_1 decreases and k_2 increases as the multiple set model type changes from high D to high I . These changes become more obvious as the number of members in the sets increases. Tables 7 and 8 list the Kissinger reaction kinetics parameters, E_K and A_K , generated from equation 13 for the two evaluations, A2/ F_n and A3/ F_n , respectively. With a low number of members in the set, E_K and A_K remain fairly constant. With increase in the number of members, as the model type changes from high D to high I , so E_K and A_K decrease from relatively high to the low values exhibited by the low number member sets.

Discussion

If the correct form of the integral equation [7a, 8] for $F(\alpha)$ and the resulting $f(\alpha)$ function are used instead of equations 9a and 6a, the relative positions of the individual curves in Figs 1a and 1b are slightly different. However, for $n' = 2$ and 3, this has little effect on the various multiple reaction sets modelled in this analysis. One finds that all α_{\max} , $\dot{\alpha}_{\max}$ and hence, calculated n -values are little affected. T_{\max} values are lower by $\sim 13 - 15^\circ$, and all $1 - \alpha$ vs. T and $\dot{\alpha}$ vs. T curves are displaced by this amount down the temperature axis. The positions and magnitudes of the linear n vs. $\ln \beta$ plots in Figs 5 and 6, and the characteristic E_F vs. α plots shown in Figs 7-10, are essentially the same.

The original Avrami-Erofeev models (A2, A3) considered two and three dimensional random nucleation as the solid state reaction rate-controlling step [8]. In discussing the generalized expression, (6a), Sestak [7b] employs the symbols G1-G7 to denote several postulated nucleation-related phenomena with Avrami exponents, $n' = 1, 1.5, 2, 2.5, 3, 4$ and 5. Consideration of the single reaction extent and rate data shown in Fig. 1a, b indicates that calculation of the Avrami exponent, n' , by measurement of α_{\max} from equation 7a, using an iterative procedure [6] can give rise to erroneous values.

As previously indicated, although the Kissinger - and Friedman- derived activation energies and pre-exponential factors for the A2 master reaction are very close to the correct values, such is not the case for the A3 master reaction, (see Table 1). It should not be forgotten that, as shown in Table 2, a number of widely disparate Avrami-Erofeev reaction kinetics parameters yield essentially superimposable extent and rate of reaction - temperature curves, shown in Figs 1c and 1d. This data, when interpreted as an n^{th} order reaction, yields comparable E_A , A_A , n values. So also the extent and rate of reaction - temperature data for both the A2 and A3 master reactions yields comparable Kissinger and Friedman reaction kinetics parameters, shown in Table 1.

The findings of this study of multiple Avrami-Erofeev type reactions, indicate that, as regards experimental investigations, an n^{th} order Arrhenius analysis of non-isothermal data at one heating rate should be performed initially. The second criterion [6] for a multiple process is examined by calculating the F_n reaction order by the two means, one valid strictly for a single reaction, the other, employing equation 7b which, although not strictly correct, is considered to be applicable to multiple reactions [6]. If the two

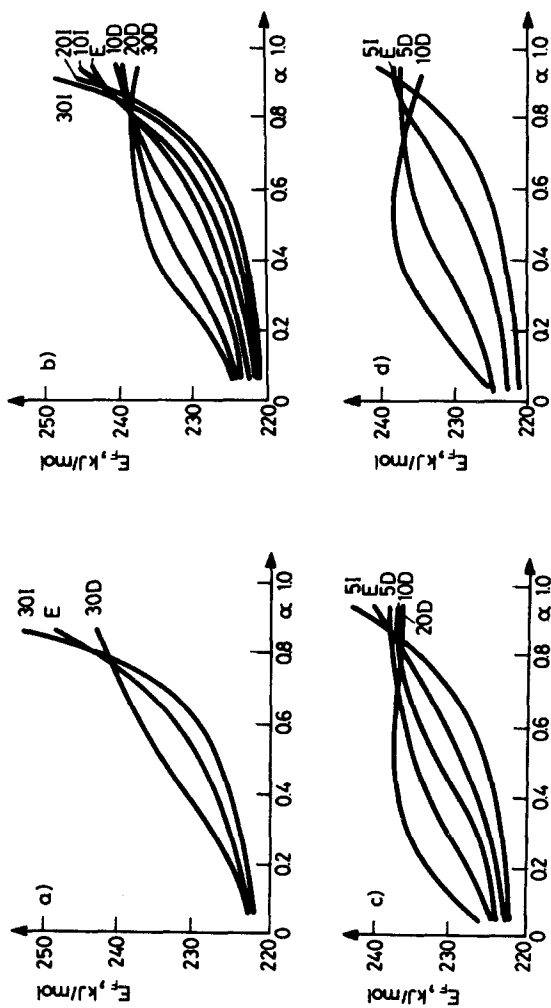


Fig. 9 E_f vs. α model A3 sets/A3 analyses. Various extent of reaction vs. temperature curve spacing. (a) 5 members (b) 10 members (c) 25 members (d) 50 members

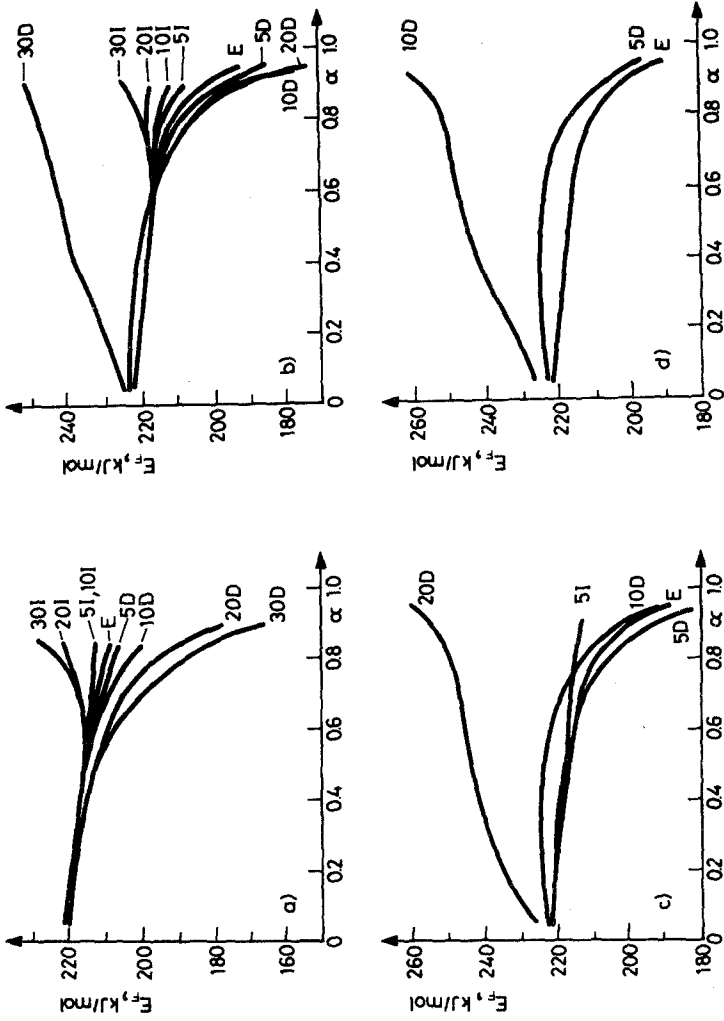


Fig. 10 E_f vs. α model A3 sets/ F_n analyses. Various extent of reaction vs. temperature curve spacing. (a) 5 members (b) 10 members (c) 25 members (d) 50 members

Table 5a. Friedman data: Compensation law parameters - model A2/A3 evaluation

No. of members	Model	$k_1 \cdot 10^2$	k_2	No. of members	Model	$k_1 \cdot 10^2$	k_2
5A2	30D	8.9904	7.8993	10A2	30D	9.2645	7.2321
	20D	9.2236	7.3761		20D	9.5682	6.5545
	10D	9.3479	7.0705		10D	9.1887	7.4794
	5D	9.3061	7.1659		5D	9.1740	7.5105
	E	9.1281	7.5936		E	9.3838	7.0203
	SI	9.1451	7.5414		SI	9.3047	7.2301
	10I	9.2744	7.2483		10I	9.0106	7.9030
	20I	9.7530	6.1751		20I	9.0238	7.8771
	30I	9.7837	6.0912		30I	9.4652	6.8879
	25A2	20D	9.7093		6.1071	50A2	10D
10D		9.5302	6.6460	5D	9.6240		6.4244
5D		9.4049	6.9693	E	9.5249		6.7422
E		9.3219	7.1867	SI	9.7905		6.2043
SI		9.4202	7.0118				
10I		9.4281	7.0199				

Table 5b. Friedman data: Compensation law parameters - model A2/A3 evaluation

No. of members	Model	$k_1 \cdot 10^2$	k_2	No. of members	Model	$k_1 \cdot 10^2$	k_2
5A3	30D	9.2400	7.3845	10A3	30D	9.8222	6.0475
	20D	8.9217	8.1152		20D	8.9354	8.0996
	10D	8.8309	8.3315		10D	9.0678	7.7969
	5D	8.7230	8.5638		5D	9.1363	7.6292
	E	9.2947	7.2674		E	8.7726	8.4806
	5I	9.4785	6.8357		5I	8.6721	8.7238
	10I	9.3250	7.2092		10I	9.5329	6.7583
	20I	9.4909	6.8164		20I	8.9908	7.9923
	30I	9.3385	7.1479		30I	9.4289	7.0005
	25A3	20D	9.4370		6.8536	50A3	10D
10D		9.1663	7.5470	5D	8.7903		8.4062
5D		9.2270	7.4379	E	9.3912		7.0973
E		9.0598	7.8448	5I	9.3856		7.1406
5I		9.2153	7.4850				

Table 6a. Friedman data: Compensation law parameters - model F_n evaluation

No. of members	Model	$k_1 \cdot 10^2$	k_2	No. of members	Model	$k_1 \cdot 10^2$	k_2	
5A2	30D	9.4043	6.2181	10A2	30D*	23.0730	-26.1978	
	20D	9.0841	7.0018		20D		8.0392	9.3990
	10D	8.3559	8.6813		10D		7.9815	9.4754
	5D	8.0794	9.3144		5D		7.5260	10.4797
	E	7.7576	10.1222		E		5.6824	14.5574
	SI	7.7338	10.1553		SI		3.2896	19.8602
	10I	7.8348	9.9774		10I		-0.5855	28.412
	20I	7.9093	9.9215		20I		-3.5656	35.0936
	30I	8.2814	9.1352		30I		-27.4554	87.4564
	25A2	20D*	16.2136		-10.0228	50A2	10D*	16.4051
10D		6.1398	13.9578	5D			40.3552	-64.0461
5D		7.9935	9.4679	E			5.9534	14.0397
E		6.3321	13.1537	SI			-25.5208	83.3652
SI		-16.2451	62.9396					
10I		-28.5714	90.1258					

*Exception

Table 6b. Friedman data: Compensation law parameters - model F_{Tz} evaluation

No. of members	Model	$k_1 \cdot 10^2$	k_2	No. of members	Model	$k_1 \cdot 10^2$	k_2
5A3	30D	8.8231	7.4044	10A3	30D*	23.7328	-26.9244
	20D	8.5637	7.9975		20D	7.4717	10.4925
	10D	7.6907	10.0101		10D	7.1537	11.1447
	5D	7.1256	11.3144		5D	5.9943	13.6942
	E	6.5667	12.5543		E	4.5297	16.9360
	5I	6.3273	13.1031		5I	2.4758	21.5158
	10I	7.0637	11.5120		10I	1.3877	23.8465
	20I	5.0273	16.1054		20I	-5.6330	39.2594
	30I	6.2146	13.5895		30I	0.6341	25.6879
	25A3	20D*	19.1610		-16.8443	50A3	10D*
10D		5.8787	14.2248	5D	4.6369		17.0568
5D		7.2421	10.9551	E	5.3831		15.0643
E		5.6099	14.5499				
5I		-2.9822	13.4355				

* Exceptions

Table 7a. Kissinger analysis: reaction kinetics parameters

No. of members	Model	A2 Evaluation		Fr Evaluation	
		$E_k, \text{kJ/mol}$	$A_k \cdot 10^{-12} \text{K} \cdot \text{min}^{-1}$	$E_k, \text{kJ/mol}$	$A_k \cdot 10^{-12} \text{K} \cdot \text{min}^{-1}$
5A2	30D	221.6	1.032	222.1	5.066
	20D	221.4	1.057	222.5	5.471
	10D	221.4	1.107	222.1	5.601
	5D	221.4	1.118	222.0	5.620
	E	221.5	1.156	222.0	5.733
	5I	221.2	1.125	221.8	5.580
	10I	221.2	1.130	221.7	5.577
	20I	221.2	1.160	221.6	5.645
	30I	221.2	1.173	221.5	5.672
	10A2	30D	235.7	5.769	235.0*
20D		224.8	1.467	225.4	7.386
10D		222.8	1.235	223.5	6.268
5D		222.4	1.209	222.9	6.100
E		222.1	1.217	222.6	6.058
5I		221.8	1.204	222.3	5.957
10I		221.7	1.219	222.1	5.979
20I		221.3	1.212	221.6	5.885
30I		221.1	1.229	221.3	5.885

*Exception

Table 7b. Kissinger analysis: reaction kinetics parameters

No. of members	Model	A2 Evaluation		F _n Evaluation	
		E _k , kJ/mol	A _k 10 ⁻¹² K.min ⁻¹	E _k , kJ/mol	A _k 10 ⁻¹² K.min ⁻¹
25A2	20D	242.0	9.566	241.1*	42.360
	10D	227.6	1.992	227.9	9.665
	5D	223.8	1.357	224.4	6.850
	E	222.5	1.268	223.0	6.328
	5I	221.9	1.270	222.2	6.201
	10I	221.4	1.254	221.5	6.032
50A2	10D	241.7	9.529	241.1*	41.800
	5D	227.4	1.917	227.7	9.406
	E	222.7	1.299	223.1	6.445
	5I	221.3	1.239	221.5	5.992

*Exception

values do not agree, there is a strong possibility that the measured data is the effective result of multiple reactions in process. The magnitude of the E_A , A_A , n parameters serve as a guide as to the solid state model which should be used in a second Arrhenius analysis, and, when data at several heating rates has been monitored, in the Kissinger and Friedman analyses.

Consider the model A2, 5-member set whose equally spaced extent of reaction - temperature curves, within the narrow window, $\alpha_5 = 0.7 \alpha_1$ at $T_1(\max)$, are shown in Fig. 3a. When analyzed as an n^{th} order process, the effective reaction data yields the values, $E_A = 456.4$ kJ/mol, $A_A = 1.251 \cdot 10^{28}$ $\text{K}^{-1} \cdot \text{min}^{-1}$, $n = 0.984$. A correlation coefficient > 0.999 , together with a 0.025 standard error of the estimate attest to the linearity of the regression over the range, $\alpha_{\text{eff}} = 0-0.974$. Applying the criterion test, the reaction order calculated assuming a single reaction is 4% greater than the equation 7b value, in good accord with that proposed for the actual model. As has been pointed out previously [13], high values of the F_n kinetics parameters are typical of singular Avrami-Erofeev reactions. It appears that such is also the case for multiple reactions of the same solid state model. As indicated above, this particular 5-member set effective reaction also conforms to the general An' model, with $n' = 2$ and also $n' = 1.18$. Except in this particular case, one cannot fit effective reaction data, resulting from a set of A2 or A3 individual reactions, to the general An' model. The F_n model parameters for the three multiple sets shown in Table 4 and Fig. 2 conform to criterion 1, and the magnitude of the E_A , A_A parameters indicate that the effective data should be analyzed as the A2, A2 and A3 models, respectively, as was carried out.

The F_n reaction order of both the A2 and A3 single master reactions remains essentially constant when calculated from extent and rate of reaction data generated over a wide range of heating rates. However, such is not the case for multiple sets. In all cases, the reaction order varies linearly with the logarithm of the heating rate. As shown in Figs 5 and 6, the slope and intercept vary according to the number of members in the sets, and the type and magnitude of the relative spacing between contiguous $1 - \alpha$ vs. T curves characterizing these sets. This characteristic behaviour constitutes the third criterion for multiple reactions.

The first criterion, the variation of the Friedman reaction kinetics parameters, E_F and A_F , with the extent of the reaction, applicable to first and n^{th} order multiple sets, is confirmed for the Avrami-Erofeev class of solid state reactions. Irrespective of the solid state model used in evaluating the effective reaction data, there are very characteristic changes in E_F and,

Table 8a. Kissinger analysis: reaction kinetics parameters

No. of members	Model	A2 Evaluation		Fn Evaluation		
		E_K , kJ/mol	$A_K 10^{-12}$ K.min ⁻¹	E_K , kJ/mol	$A_K 10^{-12}$ K.min ⁻¹	
5A3	30D	221.1	1.112	221.6	3.582	
	20D	220.9	1.111	221.8	3.817	
	10D	220.9	1.146	221.6	3.841	
	5D	221.0	1.176	221.6	3.870	
	E	220.9	1.174	221.5	3.855	
	5I	220.8	1.166	221.3	3.795	
	10I	220.8	1.173	221.3	3.834	
	20I	220.8	1.200	221.2	3.839	
	30I	220.8	1.215	221.1	3.849	
	10A3	30D	229.9	3.190	229.3*	9.072
		20D	223.0	1.349	223.6	4.512
		10D	222.0	1.258	222.6	4.211
5D		221.7	1.240	222.2	4.105	
E		221.5	1.238	222.0	4.065	
5I		221.4	1.257	221.8	4.080	
20I	10I	221.1	1.222	221.4	3.966	
	20I	220.9	1.229	221.2	3.935	
	30I	220.6	1.199	220.8	3.827	

*Exception

Table 8b. Kissinger analysis: reaction kinetics parameters

No. of members	Model	A2 Evaluation		Fn evaluation	
		E_k , kJ/mol	$Ak10^{-12}$ K.min $^{-1}$	E_k , kJ/mol	$Ak10^{-12}$ K.min $^{-1}$
25A3	20D	234.7	4.743	234.1*	13.947
	10D	224.7	1.605	225.1	5.218
	5D	222.5	1.299	223.1	4.361
	E	221.6	1.235	222.0	4.087
	5I	221.3	1.266	221.6	4.075
50A3	10D	234.9	5.028	234.2*	14.519
	5D	225.0	1.688	225.3	5.429
	E	221.7	1.262	222.2	4.166
	5I	220.9	1.250		

*Exceptions

because of the compensation relationship, in A_F with α . As shown in Figs 7-10, the behaviour is different according to the model employed, A2/A3 or F_n . Thus, both models should be used in the Friedman and Kissinger analyses.

A reasonable estimate of the type of multiple set, and the number of members it contains, can be made by comparing the F_n model $n - \ln \beta$, and $E_F - \alpha$ relationships with the patterns typified in Figs 5 and 6, and Figs 8 and 10. The magnitude of the n^{th} order, E_A , A_A values resulting from an Arrhenius analysis of data at any heating rate will serve as a guide as to which model, A2 or A3, should be used in generating E_F vs. α curves. Comparison of such generated data with the characteristic shapes shown in Figs 7 and 9 will assist in confirming the investigator's hypothesis as to the possible mechanism of a potential multiple process. As the results in Tables 7 and 8 show, with the exception of the high D models, Kissinger analysis data gives a reasonable estimate of the reaction kinetics parameters of the initial reaction in a multiple set.

As the Avrami exponent approaches unity, it will become increasingly difficult to differentiate between true nucleation and simple first order reactions. Even though it may be very difficult to test for the second and third criteria, testing for the first should always be possible.

Modern DSC and TG instrumentation enables reasonably accurate temperature dependent data to be monitored, but as shown in Figs 7-10, reaction kinetics data calculated at high $\alpha \geq 0.9$ is suspect, even with the perfect control of the independent variable, temperature, in a model experiment. In attempting to utilize the findings of these multiple reaction scheme analyses to interpret experimental data, the necessity for strict sample temperature control, particularly at relatively high heating rates, $\beta \sim 10-20$ deg/min, cannot be over-emphasized. It is this aspect of thermoanalytical instrumentation development that is of most importance.

Glossary of symbols

- α extent of reaction (dimensionless)
- $d\alpha/dt$, $\dot{\alpha}$ rate of reaction (min^{-1})
- T absolute temperature (K)
- E energy of activation (kJ/mol)
- A pre-exponential factor ($\text{K}^{-1} \cdot \text{min}^{-1}$)
- R universal gas constant (8.31434 kJ/mol.K)

- β heating rate (deg/min)
- $p_1 (E/RT)$ general function including the exponential temperature integral
- η general function including E/RT and $p_1 (E/RT)$
- $\theta_1 (\alpha_{\max})$ correction term in Kissinger equation
- n exponent in all n^{th} order relationships
- n' Avrami exponent
- f number descriptive of the spacing between the extreme extent of reaction - temperature curves
- L numbers of members in a multiple reaction set
- k_1, k_2 compensation equation parameters
- Subscripts
- A -Arrhenius F -Friedman K -Kissinger

* * *

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Zusammenfassung — Es wurde eine Untersuchung der Eigenschaften von unter nichtisothermen Bedingungen mit konstanter Aufheizgeschwindigkeit generierten effektiven Reaktionen durchgeführt, die sich aus verschiedenen gewichteten Kombinationen einer Reihe von voneinander unabhängigen Einzelreaktionen ergeben, die der Avrami-Erofeev-Regel unterliegen, bei der der geschwindigkeitsbestimmende Mechanismus ein dreidimensionales Randomnucleation-Phänomen ist. Wie in vorangehenden Untersuchungen wurden unter Anwendung von Mehrfachsets aus Einzelreaktionen erster und n -ter Reaktionsordnung im Hinblick auf die Reaktionsgeschwindigkeit-Temperatur-Kurven und die Separierung der ein-

zelenen Anteile drei Modellklassen berücksichtigt. Das relative Spacing bei einer definierten Temperatur wird um ein gegebenes Inkrement entweder gesenkt, erhöht oder bleibt konstant. Es wurden Sets mit 5 bis 50 Teilreaktionen untersucht.

An den Daten der effektiven Reaktionen wurde für jede Aufheizgeschwindigkeit eine Arrhenius-Analyse durchgeführt und über einen Intervall von Aufheizgeschwindigkeiten generierte Daten wurden mittels der allgemeinen Isokonversionsnäherung von Kissinger und Friedman analysiert. Die effektive Reaktion kann als Reaktion n -ter Ordnung analysiert werden oder, wenn man die Gültigkeit der Avrami-Erofeev-Regel annimmt. Es werden einige Merkmale diskutiert, die sich aus den verschiedenen Analysen ergeben