

## MULTIPLE REACTION SCHEME MODELLING

### III Mutually independent $n^{\text{th}}$ order reactions

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Analyses of the kinetics of the effective reactions, resulting from linear combinations of a wide range of  $n^{\text{th}}$  order single reactions in a multiple set with variously chosen energies of activation and pre-exponential factors, generated under simulated non-isothermal conditions, have been carried out. The global kinetics parameters of the several models were obtained by subjecting extent and rate of reaction data, generated at a number of different linear heating rates, to Arrhenius, Kissinger and Friedman isoconversional analyses. Multiple sets, comprising from five to fifty individual members, with order varying from 0.25 to 5 have been considered. The effects of model design on the overall reaction kinetics parameters are discussed. Criteria applicable to experimental thermoanalytical data for recognition of multiple reactions are presented.

An analysis has been performed of the characteristics of the kinetics of the effective reaction resulting from a mutually independent, equal weight combination of individual  $n^{\text{th}}$  order reactions in a multiple set, under non-isothermal, constant heating rate conditions. Sets comprising five, ten, twenty-five and fifty members have been considered, with the individual member reaction orders varying from 0.25 to 5. With regard to the separation of the extent of reaction—temperature curves for the single members at one defined temperature, namely, that of the maximum rate of the first member of the set, three model classes have been examined. The spacing either decreases ( $D$ ) or increases ( $I$ ) by a set fraction of the total separation between the first and last members, or remains equal ( $E$ ). The activation energies and pre-exponential factors for the individual set members obey the Compensation Law relationship. The variation of the effective reaction order with model class, and number and order of members in the set has been examined. Data generated at several heating rates has been subjected to Kissinger and Friedman-isoconversional analyses. For models with  $n < 1$ , the effective reaction order is highly dependent upon the model spacing, and more importantly, the number of members in the set. For a 0.75 reaction order, the effective reaction order

can vary from 2 to 0.6 as the number of members increases from five to fifty. With the exception of  $D$  models, the Friedman activation energy decreases essentially in a linear manner with extent of reaction up to 0.6. With increase in individual member reaction order, this negative change gradually lessens, eventually becoming positive. For all  $D$  models, the Friedman-derived reaction kinetics parameters increase monotonically with extent of reaction, irrespective of the individual member reaction order. In all cases, the Friedman-derived reaction kinetics parameters obey the Compensation Law.

The modelling of multiple thermally stimulated reactions in the solid state in terms of a set of singular reactions is in its early stages. Thus, with possibly few exceptions, all models have assumed that each individual physico-chemical reaction follows the most simple reaction kinetics law, namely, that of first order.

In considering the overall reaction resulting from a set of mutually independent first order reactions, both Flynn [1] and Ozawa [2] employed singular reactions with widely disparate reaction kinetics parameters; energy of activation ( $E$ ) and pre-exponential factor ( $A$ ) in the rate equation. Furthermore, the number of members in the sets were limited to less than five. The general consensus is that, in the real world the size of such sets could be very large. This is particularly so when the pyrolytic or oxidative degradation of naturally occurring substances, such as ligno-cellulosic materials [3], or fossil fuels, see for example, Elder [5], are considered. Since, in such complex materials, many of the singular reactions occurring may be so similar, then too, the individual  $E$  and  $A$  values characterizing the reaction kinetics may be comparable.

Elder [4, 5] has considered such multiple set models, consisting of a large number of mutually independent, first order reactions with close-valued reaction kinetics parameters. It has been shown [5] that the order of the effective reaction, generated under constant heating rate conditions from these singular reactions, can vary from as low as 0.6 to as high as 3.0. The individual  $E_i$  and  $A_i$  values of each member of the set control the position of the generated extent and rate of reaction curves on the temperature axis. The relative spacing between the individual curves and the number of members in the multiple set determine the value of the effective reaction order. Friedman analysis, namely, iso-conversional Arrhenius analysis of non-isothermally generated DSC and TG data, is receiving increasing interest. In this procedure, as has recently been shown [6], as far as the calculation of the activation energy of a single reaction is concerned, the form of the  $f(\alpha)$  function in the rate equation, i.e. the type of reaction kinetics model used, is irrelevant. For this reason, its use is being increasingly advocated, since Arrhenius analysis of a single set of experimental data, generated at one heating rate, can yield widely different  $E$  and  $A$  values, depending upon the chosen reaction kinetics model [6].

The procedure for parameter selection of the individual members of a mutually

independent multiple set, discussed in the second paper of this series [5], has been extended to cover singular reactions obeying other kinetics laws, e.g. those in which diffusion, or random nucleation or phase boundary movement are rate-controlling. It is known from preliminary examinations that the effective data resulting from multiple sets of such processes may be analysed as  $n^{\text{th}}$  order reactions. Prior to carrying out a detailed examination of these classes of multiple reaction sets, it is considered necessary first to consider  $n^{\text{th}}$  order reactions in general.

Summarizing the parameter selection procedure [5], a multiple set is generated by moving the extent ( $\alpha$ ) and rate ( $\dot{\alpha}$ ) of reaction—temperature curves of a master reaction, with known parameters [ $E_1$ ,  $A_1$ ,  $n$ ], along the temperature axis. The parameters of each temperature-displaced extent and rate of reaction set are obtained by Arrhenius analysis. Since the separation  $\Delta\alpha(\Delta\dot{\alpha})$  between any two adjacent curve sets differ according to the temperature, one temperature, namely, that of the maximum rate,  $\dot{\alpha}(\text{max})$ , of the master reaction,  $T_1(\text{max})$ , is chosen by which to define the desired separation.

In order to generalize the different possible arrangements of individual extent and rate of reaction curves on the temperature axis, three classes of multiple sets may be generated. The separation,  $\Delta\alpha$ , between the members either decreases or increases incrementally, or remains constant, within an envelope defined by the first and last member of the set. The last member is chosen such that, at  $T_1(\text{max})$ ,  $\alpha_L/\alpha_1$  is small. It has been shown that, in the case of multiple sets of first order reactions, the effective reaction order can vary from 1.0 to  $\sim 2.5$  as the width of the envelope increases. However, there is a limit to the magnitude of the width.

Effective rate of reaction—temperature curves with a single maximum result only if  $\alpha_L/\alpha_1 \geq 0.05$ . This also holds true for multiple  $n^{\text{th}}$  order reaction sets. This limiting ratio has been used throughout in this analysis, in order to generate the most widely ranging effects. The most dramatic variations in the order of the effective reaction, resulting from multiple first order reaction sets, are shown for those comprising from fifteen to fifty members in which the relative spacing,  $\Delta\alpha$ , between continuous member extent of reaction—temperature curves decreases by 15–30%.

The most important result of the analyses of multiple first order reaction sets is that the Friedman  $E_F$  and  $A_F$  kinetics parameters, obtained by iso-conversional Arrhenius analysis of the effective reaction data, can vary substantially with the extent of the effective reaction. This is particularly so when large number sets,  $\geq 25$  members, with decrementally spaced individual extent of reaction—temperature curves are considered.

It is the purpose of this paper to demonstrate the consequences of employing  $n^{\text{th}}$  order singular reactions in the multiple sets on the characteristics of the effective reaction, and to present the results of Friedman analyses of the overall data. In order to achieve this, multiple sets, consisting of five to fifty member singular

reactions, with a wide range of orders, from 0.25 to 5.0, belonging to the three curve separation classes, have been examined.

### Theoretical basis

All reactions, both singular and effective, resulting from a mutually independent, equal weight combination of the individual members of the set, are assumed to follow the solid state reaction rate law (1) with the temperature exponent,  $m = 1$ , and the  $f(\alpha)$  function given by (2).

$$d\alpha/dt = A \cdot T^m \cdot \exp(-E/RT) \cdot f(\alpha) \quad (1)$$

$$f(\alpha) = (1 - \alpha)^n \quad (2)$$

Details of the basic reaction kinetics modelling program, KINMOD, and the multiple set individual member parameter selection program, PARCAL, both written in Fortran 77, are given in the first two papers of this series [4, 5]. Utilizing the individual  $E_i$ ,  $A_i$  values, generated by PARCAL, KINMOD enables:

(a) the generation of each singular reaction, and the normalized effective reaction, extents and rates of reaction as functions of temperature over the range,  $\alpha_{\text{eff}} = 0.001$  to 0.999;

(b) the calculation of the effective order of reaction, 'n', which is related to the extent,  $\alpha_{\text{max}}$  at the maximum rate,  $\dot{\alpha}_{\text{max}}$  of the effective reaction by (3) where the  $\eta$ -function related to the  $p_1(x)$  function, is given by (4). The  $p_1(x)$  is the well-known function which includes the exponential temperature integral [7], and  $x = E/RT_{\text{max}}$ .

$$\alpha_{\text{max}} = 1 - [1 - \eta \cdot (n - 1)/n]^{1/(n-1)} \quad (3)$$

$$\eta = (1 + 1/x) \cdot p_1(x) \cdot x^3 \cdot e^x \quad (4)$$

(c) an Arrhenius analysis of the overall reaction data, generated at several linear heating rates in the range 1–150 deg min<sup>-1</sup>;

(d) a generalized Kissinger analysis of the maximum reaction rate data [6];

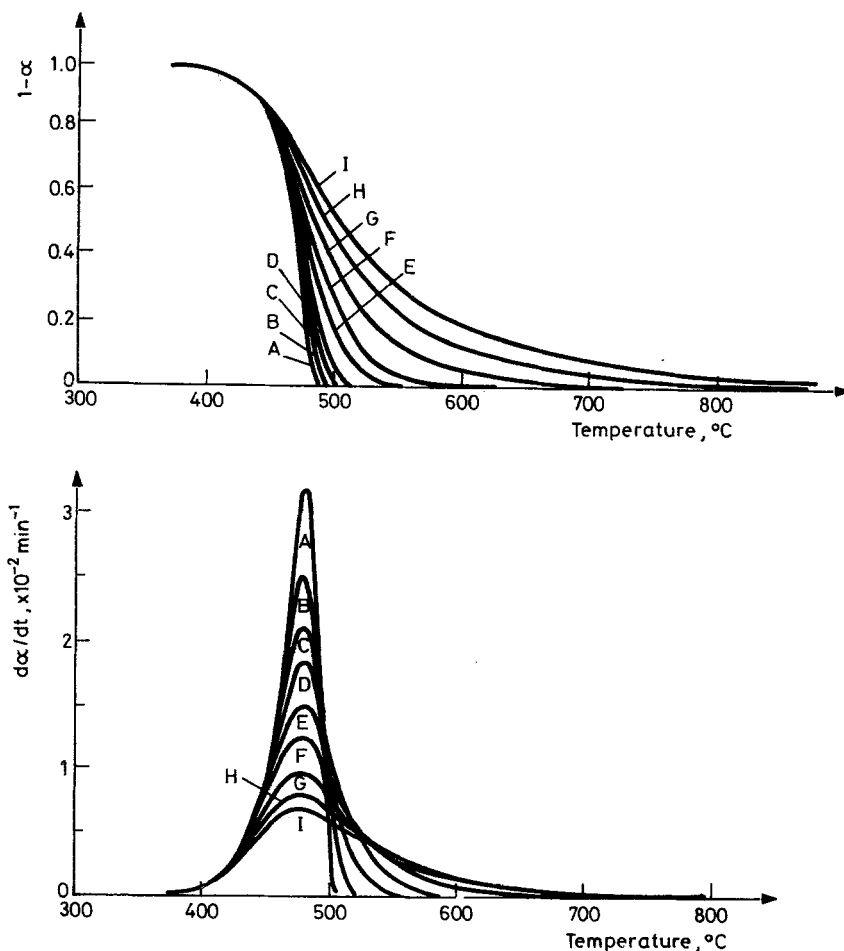
(e) a Friedman analysis using the entire set of effective data at  $\alpha_{\text{eff}} = 0.05$  to 0.95 at 0.05 intervals.

In the following analysis, a simple alphanumeric code will be used to identify the type of multiple set being considered. The number indicates the percentage change in the separation of contiguous extent of reaction—temperature curves, and the letter describes the manner by which the separation changes, decrementally (*D*), incrementally (*I*), or equally (*E*). For example, 30*D* indicates a multiple set in which the individual extent of reaction—temperature curves close rapidly, the separation decreasing by 30%. A 5*I* set is one in which the curves open more gradually, the separation increasing by 5%. In an equally spaced set, the separation is defined by

the number of members, and the code number indicates the percentage of the total spacing between the first and last members. Thus, for example, a 10-member set with nine equally separated spacings, confined within a  $\alpha_{10}/\alpha_1$  envelope of 0.05, is referred to as 10.56E.

### Analytical results

As in previous work [4, 5], the parameters  $E_1 = 220 \text{ kJ}\cdot\text{mol}^{-1}$  and  $A_1 = 1.250 \cdot 10^{12} \text{ K}^{-1}\cdot\text{min}^{-1}$  are used for the master reaction throughout this analysis. Figure 1 shows the complement,  $1-\alpha$ , and the rate,  $\dot{\alpha}$ , of reaction as a



**Fig. 1** Complement of the extent and rate of reaction—temperature relationships at  $10 \text{ deg}\cdot\text{min}^{-1}$ .  $E_1 = 220 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $A_1 = 1.250 \cdot 10^{12} \text{ K}^{-1}\cdot\text{min}^{-1}$ ,  $n = 0.25$  (A), 0.5 (B), 0.75 (C), 1.0 (D), 1.50 (E), 2.0 (F), 3.0 (G), 4.0 (H), 5.0 (I)

function of temperature for this master reaction with varying values of the order,  $n = 0.25$  to  $5.0$ , generated at a  $10 \text{ deg min}^{-1}$  heating rate. Although  $T_{\max}$  decreases only very slightly from  $479.4^\circ$  ( $n = 0.25$ ) to  $475.0^\circ$  ( $n = 5.0$ ), both  $\alpha_{\max}$  and  $\dot{\alpha}_{\max}$  decrease markedly with increase in order. For single reactions, the order may be calculated from (5).

$$n = \beta \cdot (1 - \alpha_{\max}) \cdot (m + E/RT_{\max}) / (\dot{\alpha}_{\max} \cdot T_{\max}) \quad (5)$$

With  $m = 1$ , the data shown in Fig. 1 is consistent with Eq. (5).

Table I lists the individual  $E_i$ ,  $A_i$  values for three different 10-member multiple sets,  $30D$ ,  $n = 0.75$ ;  $10.56E$ ,  $n = 1.5$ ; and  $5I$ ,  $n = 2.0$ . All the sets obey the compensation law (6), with  $k_1$  and  $k_2$  given in Table I.

$$\ln A_i = k_1 \cdot E_i + k_2 \quad (6)$$

As can be seen for model  $A$ ,  $\Delta T_{\max}$  between contiguous reactions decreases from  $9.7$  to  $5.1^\circ$  indicative of the 30% decremental spacing, while for model  $C$ ,  $T_{\max}$  increases from  $3.2$  to  $22.6^\circ$ , showing the 5% incremental spacing. Since the

**Table I** 10 member multiple set data at  $10 \text{ deg} \cdot \text{min}^{-1}$

A			B			C		
30D $n = 0.75$			10.56E $n = 1.5$			5I $n = 2.0$		
$E_i$ , $\text{kJ} \cdot \text{mol}^{-1}$	$A_i \cdot 10^{-12}$ , $\text{K}^{-1} \cdot \text{min}^{-1}$	$T_{\max}$ , $^\circ\text{C}$	$E_i$ , $\text{kJ} \cdot \text{mol}^{-1}$	$A_i \cdot 10^{-12}$ , $\text{K}^{-1} \cdot \text{min}^{-1}$	$T_{\max}$ , $^\circ\text{C}$	$E_i$ , $\text{kJ} \cdot \text{mol}^{-1}$	$A_i \cdot 10^{-12}$ , $\text{K}^{-1} \cdot \text{min}^{-1}$	$T_{\max}$ , $^\circ\text{C}$
220.0	1.250	478.6	220.0	1.250	478.0	220.0	1.250	477.4
226.4	2.170	488.3	222.3	1.505	481.8	221.9	1.441	480.6
231.7	3.392	496.4	224.7	1.836	485.6	224.1	1.725	484.1
236.6	5.101	503.8	227.3	2.250	489.7	226.4	2.071	487.8
241.3	7.541	510.6	230.0	2.805	494.0	229.0	2.548	491.9
245.8	10.964	517.1	233.1	3.589	498.9	232.0	3.237	496.6
250.1	15.678	523.2	236.8	4.807	504.5	235.6	4.367	502.3
254.1	21.435	529.0	241.5	7.021	511.6	240.4	6.388	509.4
257.9	29.241	534.4	248.4	12.417	521.7	247.5	11.414	519.9
261.4	38.421	539.5	262.6	38.702	541.8	263.5	41.422	542.5
$k_1 = 0.0827$			$k_1 = 0.0865$			$k_1 = 0.0869$		
$k_2 = 9.681$			$k_2 = 10.11$			$k_2 = 10.09$		
$E_{\text{eff}}$ , $\text{kJ} \cdot \text{mol}^{-1}$	$A_{\text{eff}} \cdot 10^{-11}$ , $\text{K}^{-1} \cdot \text{min}^{-1}$	$n_{\text{eff}}$	$E_{\text{eff}}$ , $\text{kJ} \cdot \text{mol}^{-1}$	$A_{\text{eff}} \cdot 10^{-12}$ , $\text{K}^{-1} \cdot \text{min}^{-1}$	$n_{\text{eff}}$	$E_{\text{eff}}$ , $\text{kJ} \cdot \text{mol}^{-1}$	$A_{\text{eff}} \cdot 10^{-11}$ , $\text{K}^{-1} \cdot \text{min}^{-1}$	$n_{\text{eff}}$
221.6	3.948	1.29	225.4	1.273	1.93	222.6	7.928	2.28
$\alpha_{\max} = 0.5626$			$\alpha_{\max} = 0.4814$			$\alpha_{\max} = 0.4474$		
$\dot{\alpha}_{\max} = 0.1323 \text{ min}^{-1}$			$\dot{\alpha}_{\max} = 0.1217 \text{ min}^{-1}$			$\dot{\alpha}_{\max} = 0.1062 \text{ min}^{-1}$		
$T_{\max} = 507.0^\circ\text{C}$			$T_{\max} = 495.6^\circ\text{C}$			$T_{\max} = 495.8^\circ\text{C}$		
1.49			2.01			2.42		

indicated separation between contiguous extent of reaction—temperature curves occurs only at  $T_{\max}$  of the master reaction, these  $\Delta T_{\max}$  values are only demonstrative of the changing separation. This is the reason the  $\Delta T_{\max}$  values for model *B* are not equal but slowly increase from 3.8 to 20.1°. For all models, irrespective of the number of members, and curve separation class, the parameter values of the final member are as shown in Table 2. As can be seen, there is a slight

**Table 2** Multiple set final member reaction kinetics parameters

$n_{\text{ind}}$	10 °C·min <sup>-1</sup>		150 °C·min <sup>-1</sup>	
	$E$ , kJ·mol <sup>-1</sup>	$A \cdot 10^{-13}$ , K <sup>-1</sup> ·min <sup>-1</sup>	$E$ , kJ·mol <sup>-1</sup>	$A \cdot 10^{-13}$ , K <sup>-1</sup> ·min <sup>-1</sup>
0.50	261.0	3.869	263.9	3.794
0.75	261.4	3.842	264.4	3.790
1.00	261.6	3.700	265.2	4.016
1.25	261.8	3.618	265.9	4.224
1.50	262.6	3.870	266.6	4.476
3.00	265.0	4.716	269.2	5.428
5.00	266.8	5.400	271.0	6.069

increase with increase in the value of the order of the individual member reactions. Furthermore, it should be noted, the values and those of the interim members, are dependent upon the heating rate. As previously indicated [5], for multi-heating rate calculations, the individual member  $E_i$ ,  $A_i$  values are generated by program PARCAL at the upper heating rate to be used in the Kissinger and Friedman analyses in program KINMOD. Consistent with previous analyses [4, 5], 150 deg min<sup>-1</sup> is used throughout; the  $E_L$ ,  $A_L$  values are indicated in Table 2. For the data summarized in Table 1, a 10 deg min<sup>-1</sup> heating rate was used in both programs. In computing the overall reaction kinetics parameters,  $E_{\text{eff}}$  and  $A_{\text{eff}}$  by linear regression of the logarithmic form of the rate Eq. (1), the regression is terminated when a deviation from linearity exceeds a certain limit, as previously explained [5]. Very often a 1% limit is too great a restriction. For example, for models *A* and *C*, regression termination occurred at  $\alpha = 0.276$  and 0.286, respectively. However, such early termination has only a small effect on the resulting overall reaction kinetics parameters. For model *A*,  $E_{\text{eff}} = 225.6$  kJ·mol<sup>-1</sup>,  $A_{\text{eff}} = 8.472 \cdot 10^{11}$  (K<sup>-1</sup>·min<sup>-1</sup>), slightly greater than the values given in Table 1. For model *C*, the effective parameters,  $E_{\text{eff}} = 222.6$  kJ·mol<sup>-1</sup>,  $A_{\text{eff}} = 8.088 \cdot 10^{11}$  (K<sup>-1</sup>·min<sup>-1</sup>) are exceedingly close to the Table 1 values. As a matter of course, the limit is always set such as to utilize the maximum amount of effective data. For models *A*, *B* and *C*, the limits were 4%, 8% and 8% resulting in regression termination at  $\alpha > 0.94$ , yielding the tabulated overall reaction kinetics parameters.

The  $n_{\text{eff}}$  values of 1.29, 1.93 and 2.28, for the three models were obtained using an iterative procedure to solve Eq. (3). Using the tabulated values of  $\alpha_{\text{max}}$ ,  $\dot{\alpha}_{\text{max}}$ ,  $T_{\text{max}}$  and  $E_{\text{eff}}$  with Eq. (5) results in significantly different values of 1.49, 2.01 and 2.42 for the three models. The differences are outside the limit resulting from even large inaccuracies in the calculated parameters. For example, an effective order of 1.29 for model *A* requires  $E_{\text{eff}} = 191 \text{ kJ} \cdot \text{mol}^{-1}$  and  $A_{\text{eff}} = 3 \cdot 10^9 \text{ (K}^{-1} \cdot \text{min}^{-1})$ . Since  $\dot{\alpha}_{\text{max}}$  is the sole parameter not used in both calculations by Eqs (3) and (5), its value was computed by a different means. The entire set of effective reaction rates were determined by employing a modification of the cubic spline technique, previously used by the author [8] to calculate reaction rates from experimental TG data. For example, for model *A*, this procedure yielded the following:  $\alpha_{\text{max}} = 0.5630$ ,  $\dot{\alpha}_{\text{max}} = 0.1363 \text{ min}^{-1}$  at  $T_{\text{max}} = 507^\circ$ , in excellent agreement with the values given in Table 1. Thus, the correctness of generating effective data by normalized summation of the individual member extents and rates of reaction has been verified. Furthermore, the differences in the calculated  $n_{\text{eff}}$  values are real. The implications of these findings will be discussed later.

Figure 2 summarizes the results of a series of similar calculations, at a heating rate of  $10 \text{ deg min}^{-1}$ , on the three classes of multiple sets comprising  $L = 5, 10, 25$  and  $50$  members. The effective order is plotted against the order of the individual member reactions, from  $n_{\text{ind}} = 0.25$  to  $5.0$ . Curve groups *a1* and *a2* refer to models *5D* and *30D*, respectively, while curve groups *c1* and *c2* are for *5I* and *30I* models. In contrast to these skewed distributions of single extent of reaction—temperature curves, *b* shows the results for the symmetrical, equally spaced curves. As previously indicated [5], single reaction  $A_i$  values may be generated by PARCAL for equally separated  $E_i$  values, where  $E_i = E_1 + (i - 1) \cdot \Delta E$ . Provided  $E_L$  lies within the limits indicated in Table 2, any  $\Delta E$  may be chosen, and effective reactions can be generated and analysed by KINMOD, as in the first paper in this series [4]. In Fig. 2, on the curves for 5-member sets, the crosses (\*) indicate the effective reaction order resulting from single member reactions in which the  $E_i$  values were obtained with  $\Delta E$  set at best fit values within the  $\alpha_1 - \alpha_5$  window at  $T_1(\text{max})$ , namely 9.9, 10.4, 10.9 and  $11.7 \text{ kJ} \cdot \text{mol}^{-1}$  for  $n = 0.25, 1, 2$  and  $5$ , respectively. Such sets are referred to as fixed as opposed to the variable  $E_i, A_i$  sets. As can be seen, irrespective of the manner by which the  $E_i, A_i$  values are generated, the variation of  $n_{\text{eff}}$  with  $n_{\text{ind}}$  is essentially the same. Similar close agreement is obtained for the 10, 25 and 50-member sets. Generally speaking, it is not possible to generate a continuous effective extent of reaction—temperature curve with a single maximum reaction rate for  $n < 0.5$ . The exception, indicated in Fig. 2 *c2* is for the 50-member *30I* set. A consideration of all data generated in this analysis, indicates that the range of  $n^{\text{th}}$  order reactions of most interest is for  $0.5 \leq n \leq 0.3$ . Figure 3 shows the  $1 - \alpha$  vs.  $T$  curves, generated at  $10 \text{ deg min}^{-1}$ , for a number of 10-member, variable  $E_i, A_i$  sets,



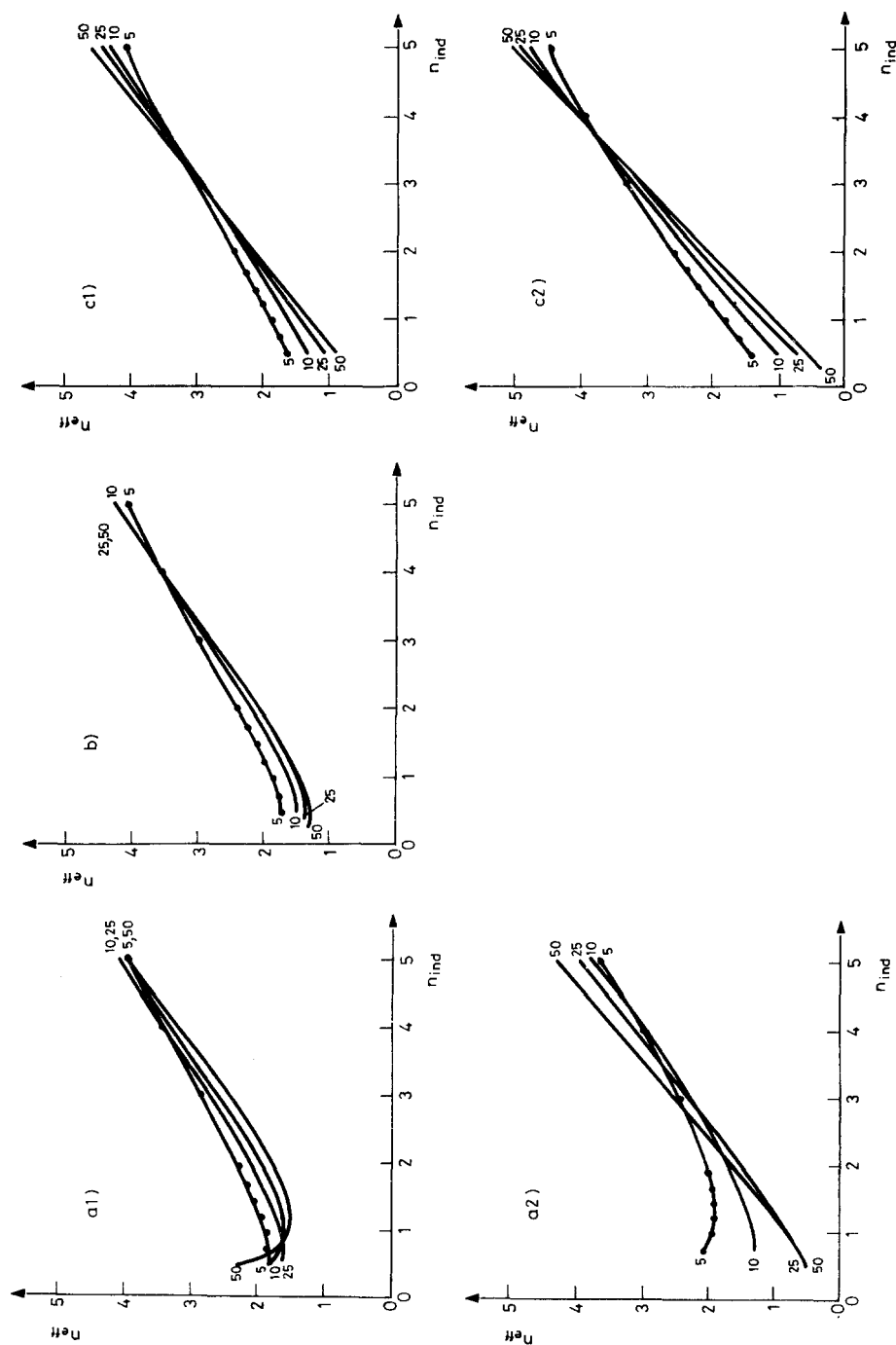


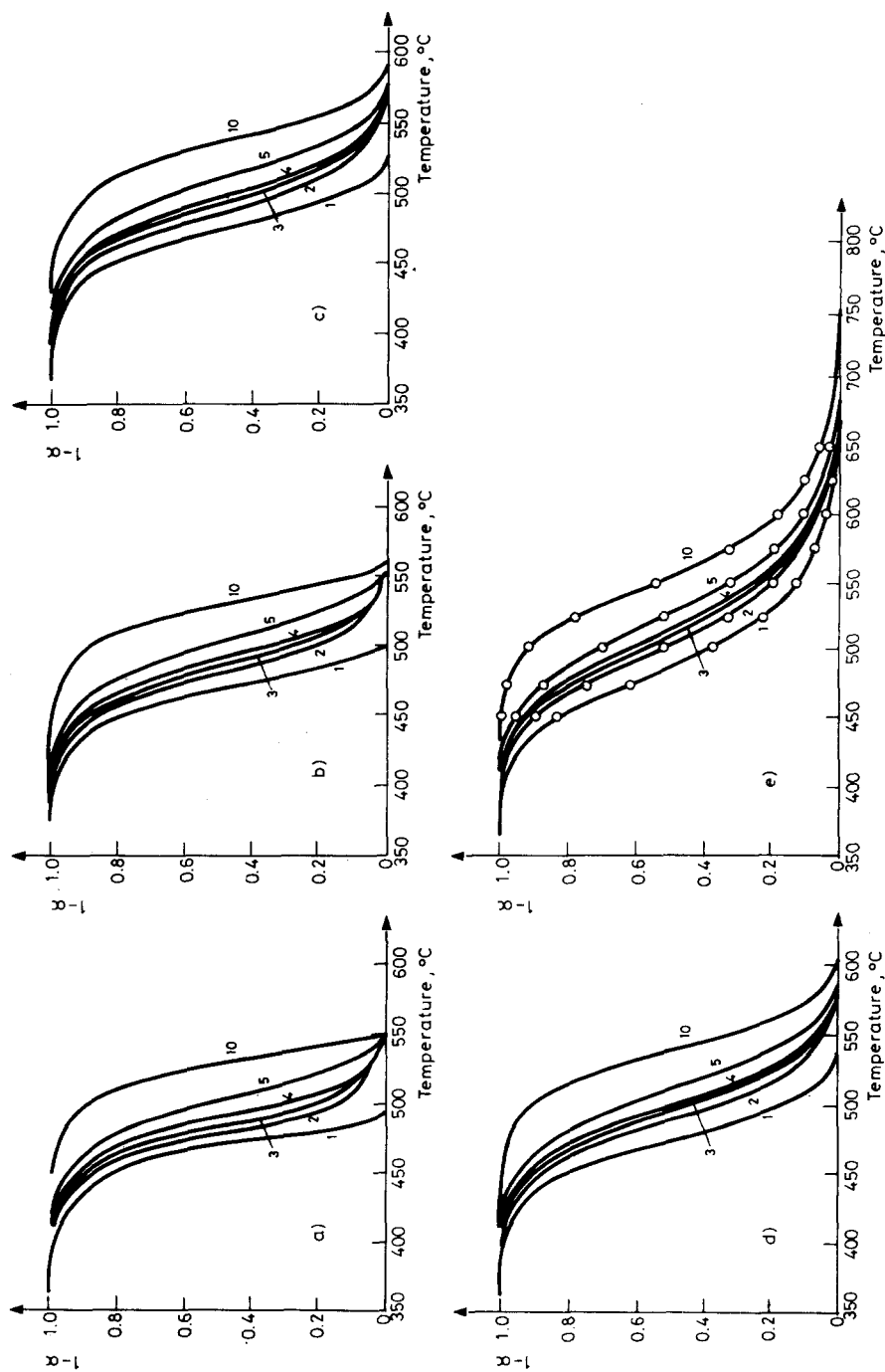
Fig. 2 Variation of the effective reaction order with the reaction order of the individual members for 5, 10, 25 and 50 member multiple sets at  $10 \text{ deg} \cdot \text{min}^{-1}$ . Models 5D (a1), 30D (a2), E (b), 5I (c1) and 30I (c2)

**Table 3** Friedman data  $E^* = k_3 + k_4 \cdot x$ 

Model	$n_{\text{ind}}$	5-member set			10-member set			25-member set		
		$k_3$	$k_4$	-end	$k_3$	$k_4$	-end	$k_3$	$k_4$	-end
30D	0.50	—	—	—	—	—	—	229.3	123.21	0.20
	0.75	225.7	-22.49	0.40	226.6	53.13	0.45	229.3	108.92	0.20
	1.00	225.9	-5.18	0.30	228.5	54.54	0.95	234.8	102.01	0.20
	1.25	226.0	7.70	0.55	231.1	47.61	0.95	236.4	98.22	0.25
	1.50	226.4	14.63	0.55	232.2	43.68	0.95	236.7	108.96	0.20
	3.00	228.7	37.35	0.60	233.5	65.39	0.40	241.0	125.78	0.15
5D	0.50	—	—	—	226.7	-23.50	0.45	228.2	-29.42	0.45
	0.75	225.2	-14.06	0.45	226.7	-12.45	0.50	228.4	-11.02	0.45
	1.00	225.2	-8.06	0.50	226.8	-3.90	0.50	228.6	-0.64	0.35
	1.25	225.2	-2.65	0.60	227.0	1.05	0.25	229.0	7.34	0.55
	1.50	225.5	0.92	0.20	227.3	4.87	0.50	229.4	12.57	0.60
	3.00	226.3	13.83	0.30	228.9	22.05	0.55	231.7	30.79	0.60
E	0.50	—	—	—	226.2	-18.99	0.50	226.8	-17.10	0.50
	0.75	225.1	-13.46	0.45	226.2	-11.07	0.50	226.7	-9.75	0.55
	1.00	225.1	-7.26	0.50	226.3	-5.11	0.55	227.0	-3.52	0.55
	1.25	225.2	-3.16	0.50	226.4	-0.51	0.60	227.1	0.60	0.45
	1.50	225.4	-0.57	0.50	226.7	2.36	0.55	227.4	3.35	0.55
	3.00	225.5	12.47	0.25	228.1	17.57	0.60	228.5	19.21	0.55
5I	0.50	—	—	—	225.7	-15.96	0.50	225.4	-11.72	0.55
	0.75	225.1	-13.04	0.45	225.7	-9.43	0.55	225.3	-7.82	0.60
	1.00	225.0	-7.20	0.50	225.8	-4.80	0.55	225.5	-4.22	0.45
	1.25	225.1	-4.48	0.45	225.9	-2.10	0.55	225.5	-1.59	0.45
	1.50	225.2	-1.15	0.40	226.1	1.07	0.40	225.6	0.51	0.60
	3.00	225.3	9.01	0.20	227.4	12.24	0.60	226.2	11.31	0.55
30I	0.50	224.2	-14.10	0.50	223.8	-8.24	0.60	221.7	-3.22	0.70
	0.75	224.3	-9.61	0.50	223.8	-5.89	0.60	221.7	-2.86	0.65
	1.00	224.3	-7.03	0.50	223.8	-4.24	0.55	221.7	-1.99	0.65
	1.25	224.4	-3.67	0.45	223.8	-2.66	0.55	221.7	-1.61	0.60
	1.50	224.5	-3.06	0.45	223.8	-1.64	0.60	221.7	-1.40	0.55
	3.00	224.9	-1.72	0.45	224.4	2.72	0.50	221.7	1.41	0.25
5.00	225.6	-10.05	0.40	224.9	8.50	0.55	221.8	4.89	0.65	

\*  $\text{kJ} \cdot \text{mol}^{-1}$ 

A ( $n = 0.5$ ), B ( $n = 0.75$ ), C ( $n = 1.25$ ), D ( $n = 1.5$ ) and E ( $n = 3.0$ ). In each diagram, the first and tenth single member curves are shown. The intermediate curves are those of the effective reactions generated for four skewed distribution sets, namely, 30I, 5I, 5D and 30D (curve numbers 2–5). In Fig. 3e, the circles indicate



**Fig. 3** Complement of the extent of reaction as a function of temperature at  $10 \text{ deg} \cdot \text{min}^{-1}$  of 10 member sets with  $n_{\text{ind}} = 0.5$  (a), 0.75 (b), 1.25 (c), 1.50 (d) and 3.0 (e). Curves 1 and 10, individual reaction data first and tenth members of the set. Models 30I(2), 5I(3), 5D(4) and 30D(5). Diagram e(0) see text for explanation

$1 - \alpha$  values for fixed  $E_i, A_i$  sets with  $\Delta E = 5$ . Again, the agreement with the variable set data is excellent.

For the low,  $n_{\text{ind}} < 1$   $5I$  and  $30I$  models, the tailing region of the effective reaction curves for  $\alpha \geq 0.85$ , is slightly distorted. This distortion disappears with increase in  $n_{\text{ind}}$ . As is seen, it is almost non-existent in the  $5D$  and  $30D$  models. For all models considered, the effective reaction curve resulting from the symmetrically spaced single member reactions lies between curves 3 and 4 in Fig. 3. This is shown for  $n = 1.5$  in Fig. 4—an expanded scale replot of Fig. 3d, the numbers 2, 3 and 4 referring to the  $5I, E$  and  $5D$  models, respectively.

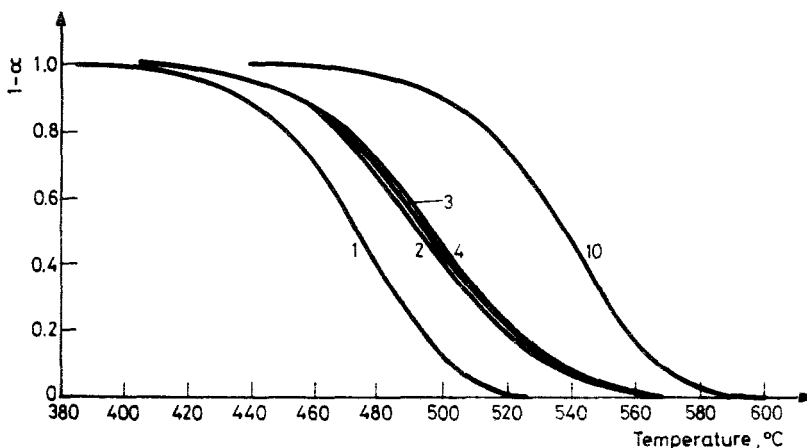


Fig. 4 Expanded scale replot of Fig. 3—diagram D, model  $5I$  (2),  $10.6E$  (3) and  $5D$  (4)

Generalized Kissinger [6] analyses of the maximum reaction rate data, and Friedman analyses of the effective extent and rate of reaction data, according to Eqs (7) and (8), and (9), respectively, over the linear heating rate range  $1-150 \text{ deg} \cdot \text{min}^{-1}$ , have been performed for a number of  $n^{\text{th}}$  order  $L$ -member sets. The Friedman analyses were carried out from  $\alpha = 0.05$  to  $0.95$  at  $\Delta\alpha = 0.05$  intervals.

$$\ln(\beta/T_{\text{max}}^3) = \ln(A_K \cdot R/E_K) + \ln \phi_1(\alpha_{\text{max}}) - E_K/RT_{\text{max}} \quad (7)$$

$$\phi_1(\alpha_{\text{max}}) = -f'(\alpha_{\text{max}})/(1+1/x) = [n - (n-1) \cdot \eta]/(1+1/x) \quad (8)$$

$$\ln[(d\alpha/dt)_x/(T \cdot (1-\alpha)^n)] = \ln A_F - E_F/RT \quad (9)$$

Figure 5 shows the Friedman activation energies,  $E_F$ , as a function of the extent ( $\alpha$ ) of the effective reaction for six 10-member sets; a ( $n = 0.5$ ), b ( $n = 0.75$ ), c ( $n = 1.25$ ), d ( $n = 1.5$ ), e ( $n = 3.0$ ) and f ( $n = 5.0$ ). Five multiple sets, models

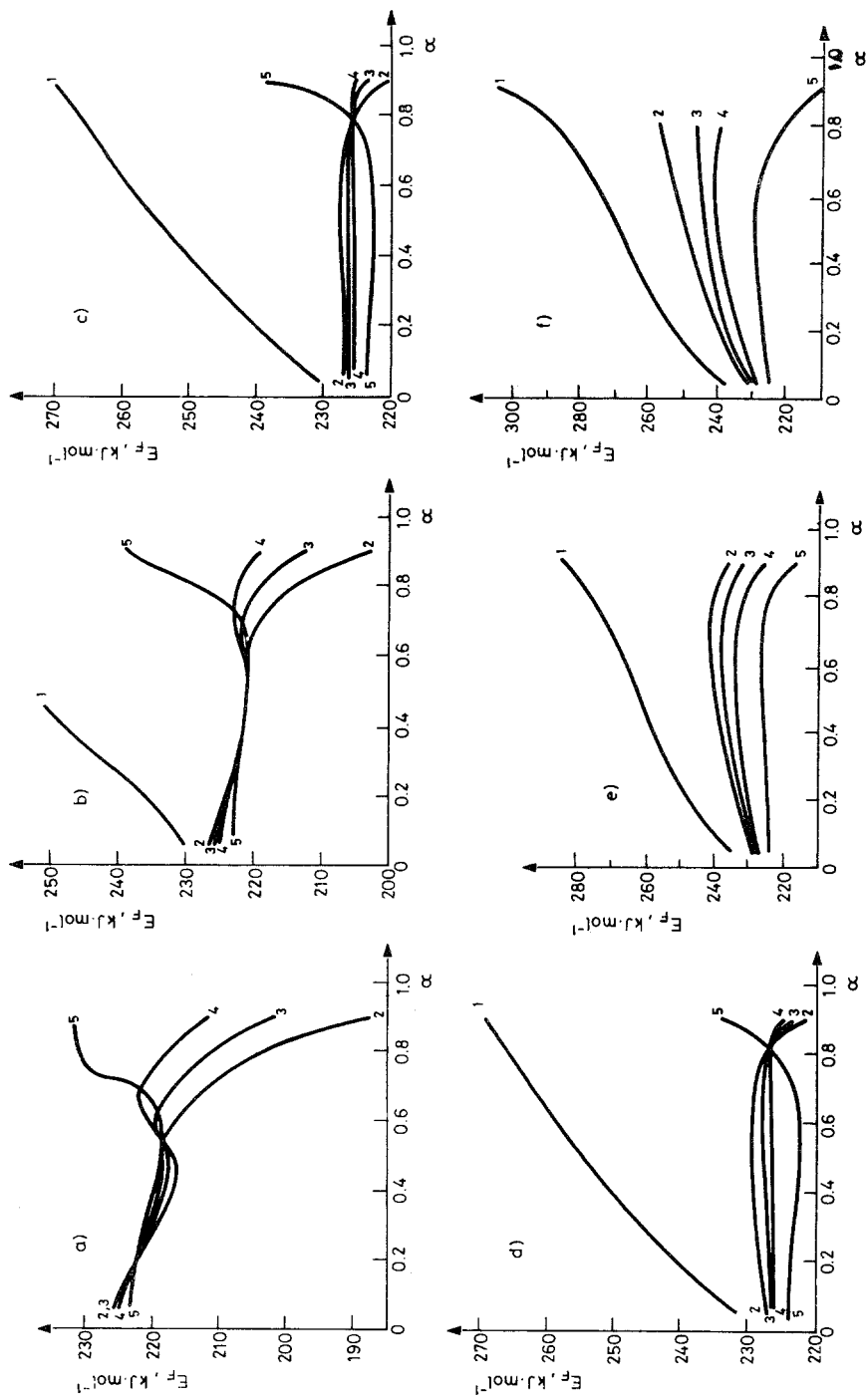


Fig. 5 Friedman analysis energies of activation as a function of extent of the effective reaction.  $n_{\text{nd}} = 0.5$  (a), 0.75 (b), 1.25 (c), 1.50 (d), 3.0 (e) and 5.0 (f). Models 30D (1), 5D (2), E (3), 5I (4) and 30I (5) – all 10 member sets

**Table 4** Friedman data  $\ln A^* = k_1 \cdot E^{**} + k_2$ 

Model	$n_{\text{ind}}$	5-member set				10-member set				25-member set			
		$k_1 \cdot 10^2$	$k_2$	#	$cc$	$k_1 \cdot 10^2$	$k_2$	#	$cc$	$k_1 \cdot 10^2$	$k_2$	#	$cc$
30D	0.50	—	—	—	—	—	—	—	—	11.284	1.824	9	0.990
	0.75	12.519	-0.395	19	0.999	14.972	-6.472	19	1.000	10.251	4.396	17	0.990
	1.00	12.152	0.323	19	0.999	12.987	-1.823	19	0.993	10.009	4.984	19	0.993
	1.25	11.090	2.661	19	0.999	11.848	0.803	19	0.999	10.003	4.980	19	0.995
	1.50	10.904	3.028	19	0.996	11.183	2.352	19	0.999	9.987	5.238	19	0.995
	3.00	8.678	8.205	15	0.995	8.976	8.159	19	0.990	9.122	7.174	17	0.992
	5.00	8.563	8.566	14	0.993	8.634	8.485	15	0.991	9.179	6.693	12	0.991
5D	0.50	—	—	—	—	12.882	-9.702	19	0.998	12.516	-0.286	19	0.999
	0.75	12.230	0.421	19	0.997	12.849	-1.019	19	0.999	12.305	0.083	19	0.999
	1.00	11.354	2.303	19	0.999	11.848	1.161	19	0.999	12.093	0.475	19	0.999
	1.25	10.225	4.787	19	0.998	11.094	2.791	19	0.998	11.376	2.068	19	0.998
	1.50	9.576	6.215	19	0.996	10.663	3.727	19	0.996	10.677	3.659	19	0.995
	3.00	12.561	-0.988	19	0.988	8.407	8.937	15	0.995	9.071	7.446	17	0.992
	5.00	5.135	16.281	9	0.995	8.374	9.051	13	0.993	8.548	8.743	15	0.991
E	0.50	—	—	—	—	13.883	-3.131	19	0.990	13.853	-3.082	19	0.995
	0.75	12.289	0.312	19	0.995	13.655	-2.744	19	0.996	13.590	-2.620	19	0.997
	1.00	11.808	1.333	19	0.999	12.155	0.526	19	0.999	12.338	0.119	19	1.000
	1.25	9.953	5.461	19	0.989	9.877	5.624	19	0.998	10.651	3.883	19	0.998
	1.50	9.546	6.532	19	0.990	9.638	6.128	19	0.996	10.422	4.363	19	0.994
	3.00	11.242	2.085	19	0.971	8.004	9.862	15	0.996	8.717	8.281	15	0.996
	5.00	14.807	-6.662	19	0.986	8.073	9.721	12	0.994	8.572	8.672	14	0.992
5I	0.50	—	—	—	—	16.622	-9.164	19	0.990	9.472	6.713	12	0.995
	0.75	12.525	-0.192	19	0.993	15.495	-6.801	19	0.971	10.112	5.262	14	0.992
	1.00	12.455	-0.077	19	0.999	12.401	0.040	19	0.988	12.165	0.662	18	0.993
	1.25	15.103	-6.083	17	0.993	9.208	7.171	19	0.981	15.909	-7.818	18	1.003
	1.50	15.697	-7.521	16	0.996	7.874	10.182	19	0.976	5.743	15.064	19	0.968
	3.00	11.597	1.293	19	0.991	7.268	11.552	15	0.992	7.900	10.184	15	0.999
	5.00	14.162	-5.056	19	0.990	7.428	11.207	12	0.992	8.025	9.917	12	0.994
30I	0.50	13.435	-2.196	19	0.916	13.486	-2.062	15	0.970	7.887	10.411	14	1.007
	0.75	12.200	0.599	19	0.984	12.696	-0.362	16	0.981	8.398	9.270	15	0.998
	1.00	12.019	1.005	19	0.995	10.962	3.458	19	0.995	11.407	2.627	19	0.999
	1.25	14.172	-3.860	18	0.999	12.944	-1.001	19	0.999	12.147	0.966	19	1.000
	1.50	15.165	-6.159	17	0.999	14.829	-5.260	19	0.997	13.085	-1.130	19	0.999
	3.00	9.761	5.624	19	0.993	8.795	8.139	19	0.993	14.994	-5.448	17	0.941
	5.00	11.730	0.629	19	0.990	11.611	1.569	19	0.986	9.372	6.997	19	0.994

\*  $\text{kJ} \cdot \text{mol}^{-1}$ \*\*  $\text{K}^{-1} \cdot \text{min}^{-1}$

30D, 5D, E, 5I and 30I (curves 1–5), have been examined. As is seen, over different extent of reaction ranges,  $E_F$  changes linearly with  $\alpha$ , according to Eq. (10). Also, over different  $\alpha$ -ranges, the Friedman pre-exponential factors and energies of activation,  $A_F$  and  $E_F$ , obey the compensation law, Eq. (6).

$$E_F = k_3 + k_4 \cdot \alpha \quad (10)$$

The values of  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$  for all the models comprising five, ten and twenty five member sets are given in Tables 3 and 4. Where values are not given, the effective reaction rate—temperature curves are multi-peaked, and the data is not amenable to analysis. Table 5 lists the Kissinger data. In generating  $k_1$  and  $k_2$  by linear regression, the regression was terminated if three deviations ( $> 2\%$ ) between the actual  $\ln A_F$  values and those calculated from Eq. (6) with  $k_1$  and  $k_2$  values from the previous stage, were observed. As is seen from the number of regression pairs used, and the high correlation coefficients (cc) shown in Table 4, with few exceptions, namely certain  $n = 3$  and  $n = 5$  models, the compensation law relationship (6) is obeyed over essentially the entire  $\alpha$ -range. In considering the Friedman analysis data, it should be emphasized that the relatively large changes observed in the  $E_F - \alpha$  curves, for  $\alpha > 0.6$ , seen in Figs 5a–5d, are just magnifications of the relatively minor distortions in the actual  $1 - \alpha$  vs.  $T$  curves, shown in this  $\alpha$ -region in Figs 3a–3d, curves 2–5.

As is to be expected, the Kissinger-derived reaction kinetics parameters follow the behaviour shown by the Friedman-derived data. For the 30D models, both  $E_K$  and  $A_K$  increase with increase in both  $L$  and  $n_{\text{ind}}$ , from close to  $E_1, A_1$  to  $E_L, A_L$  (see Table 2). These value changes lessen in the 5D and E models, and for all 5I and 30I models,  $E_K$  and  $A_K$  are very close to  $E_1, A_1$ .

## Discussion

The overall purpose of this series of papers is, by studying models of multiple reactions, to generate criteria whereby the occurrence of multiple reactions in an experimental investigation may be recognized.

As the analyses performed have demonstrated for  $n^{\text{th}}$  order reactions, two general facts have emerged. First, the value of the reaction order,  $n_{\text{eff}}$ , calculated by the two relationships, Eqs (3) and (5), differ. Secondly, the kinetics parameters as calculated by iso-conversional Arrhenius analysis, can vary with the extent of the global reaction.

General expressions, analogous to Eqs (3) and (5), cannot be derived for the effective reaction of a multiple set, since both  $\alpha_{\text{eff}}$  and  $\dot{\alpha}_{\text{eff}}$  are summations of the individual  $\alpha_i$  and  $\dot{\alpha}_i$  values, and the maximum effective reaction rate will be model-

Table 5 Kissinger data

Model	$n_{ind}$	5-member set		10-member set		25-member set	
		$E_k^*$	$A_k^{**} \cdot 10^{-12}$	$E_k^*$	$A_k^{**} \cdot 10^{-12}$	$E_k^*$	$A_k^{**} \cdot 10^{-12}$
30D	0.50	—	—	—	—	257.4	20.125
	0.75	221.6	0.775	246.1	14.364	264.9	59.781
	1.00	224.8	1.020	250.1	22.137	265.5	62.348
	1.25	227.9	1.366	248.7	15.222	265.6	61.628
	1.50	230.3	1.701	250.0	16.240	265.9	61.992
	3.00	240.7	4.747	256.1	27.601	266.9	59.970
5D	0.50	—	—	222.3	1.043	223.0	1.039
	0.75	222.4	1.006	223.9	1.132	226.1	1.328
	1.00	223.4	1.035	225.9	1.342	228.6	1.628
	1.25	224.6	1.106	227.2	1.448	231.1	2.082
	1.50	225.6	5.176	228.5	1.612	233.2	2.560
	3.00	229.1	1.322	235.3	3.062	241.4	6.041
E	0.50	—	—	222.2	1.082	223.1	1.191
	0.75	222.4	1.025	223.7	1.173	224.4	1.253
	1.00	223.5	1.079	225.1	1.281	226.1	1.454
	1.25	224.5	1.128	226.3	1.408	227.3	1.581
	1.50	225.2	1.170	227.3	1.501	228.3	1.709
	3.00	227.9	1.176	232.7	2.384	234.0	2.933
5I	0.50	—	—	222.2	1.123	222.4	1.197
	0.75	222.4	1.041	223.4	1.194	223.2	1.231
	1.00	223.4	1.096	224.6	1.286	224.4	1.369
	1.25	224.1	1.110	225.4	1.333	225.1	1.426
	1.50	224.9	1.164	226.4	1.435	225.8	1.479
	3.00	226.6	1.024	230.5	1.970	229.3	1.962
30I	0.50	221.3	1.071	221.6	1.180	220.7	1.212
	0.75	222.2	1.105	222.2	1.217	220.9	1.208
	1.00	222.7	1.112	222.8	1.248	221.2	1.241
	1.25	223.6	1.192	223.2	1.272	221.3	1.229
	1.50	223.8	1.154	223.4	1.260	221.4	1.228
	3.00	224.3	0.922	225.0	1.334	222.2	1.257

\*  $\text{kJ} \cdot \text{mol}^{-1}$ ; \*\*  $\text{K}^{-1} \cdot \text{min}^{-1}$ 

dependent. Both (3) and (5) are derived from the integral form,  $F(\alpha)$ , of the basic rate Eq. (1). The development of (3) utilizes the reaction kinetics model-independent relationship [7]  $-f'(\alpha_{max}) \cdot F(\alpha_{max}) = \eta$ , where  $\eta$ , as shown by (4) is a function only of the activation energy and the temperature at which the rate attains its maximum value. As shown in Fig. 1, whereas  $T_{max}$  varies very little with variation



in  $n$ ,  $\dot{\alpha}_{\max}$  is highly dependent on  $n$ . Therefore, it is considered that Eq. (3) rather than (5) yields the more correct value of the effective reaction order. The percentage difference,  $D$ , between  $n$ , as calculated by (5), and the value, evaluated from (3), are listed in Table 6, for five widely differing models, with  $n_{\text{ind}}$  varying from 0.75 to 3.0

$$D = 100 \cdot (n_5 - n_3) / n_3 \quad (11)$$

For large member, 30D and 30I sets ( $L \geq 25$ ), the  $E_i$  and  $A_i$  values of many of the final and initial members, respectively, are so close as to be indistinguishable. These sets have not been listed in Table 6. As can be seen for  $n \leq 1.5$ , the difference,  $D$ , initially negative, becomes less so with increase in the number of members in the set. As the skewed distribution in the  $1 - \alpha$  vs.  $T$  curves changes from decrementally to incrementally changing spacing, so the difference becomes more negative. The fact that, in carrying out an  $n^{\text{th}}$  order reaction kinetics analysis of experimental, non-isothermal DSC or TG data, results in a non-zero difference,  $D$ , in the order, as calculated by relationships (3) and (5), is the first criterion of the occurrence of a multiple reaction system. Two examples of non-isothermal experimental data will

Table 6 Multiple set model reaction order percentage differences

$n_{\text{ind}}$	#	30D	5D	E	5I	30I
0.75	5	- 7.1	- 9.6	-10.1	-10.5	-10.8
	10	+15.9	- 6.6	- 7.6	- 8.8	-10.1
	25	+24.3	- 5.3	- 6.5	- 6.7	- 4.7
	50	—	- 2.2	- 6.4	- 5.6	—
1.00	5	+ 1.1	- 3.6	- 4.3	- 4.9	- 6.9
	10	+14.0	- 1.2	- 2.0	- 2.9	- 5.7
	25	—	+ 1.1	- 1.2	- 3.0	- 3.1
	50	—	+ 5.2	- 0.9	- 3.2	—
1.50	5	+10.2	+ 3.9	+ 2.4	+ 2.0	- 0.5
	10	+16.8	+ 5.1	+ 3.9	+ 2.7	- 0.1
	25	—	+ 7.9	+ 4.5	+ 2.4	- 0.1
	50	—	+11.8	+ 4.8	+ 2.2	—
2.00	5	+13.7	+ 8.0	+ 7.2	+ 5.8	+ 4.0
	10	+12.3	+ 8.5	+ 7.2	+ 5.8	+ 2.5
	25	+ 8.0	+10.1	+ 6.5	+ 5.0	+ 0.9
	50	—	+10.0	+ 6.2	+ 3.4	—
3.00	5	+12.6	+12.1	+12.0	+11.2	+ 8.7
	10	+10.7	+ 9.4	+ 9.4	+ 8.6	+ 4.9
	25	+ 2.8	+ 8.3	+ 7.6	+ 6.4	+ 2.9
	50	—	+ 8.2	+ 7.1	+ 4.9	—

be considered as purely demonstrative of the use of this criterion. A recent investigation of the thermal degradation of calcium carbonate [9] yielded the following: at  $10 \text{ deg} \cdot \text{min}^{-1}$ ,  $\dot{\alpha}_{\text{max}} = 0.1412 \text{ min}^{-1}$  at  $\alpha_{\text{max}} = 0.7621$ ,  $T_{\text{max}} = 736^\circ$ . With  $m = 1$  in the rate equation,  $E_A = 196.1 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $n_3 = 0.39$  and  $n_5 = 0.40$ , indicating that in a finely divided, pure sample, essentially only one reaction is occurring. On the other hand, in a study of the pyrolysis of bituminous coal [10], at  $100 \text{ deg} \cdot \text{min}^{-1}$ ,  $\dot{\alpha}_{\text{max}} = 0.6 \text{ min}^{-1}$  at  $\alpha_{\text{max}} = 0.4$ ,  $T_{\text{max}} = 500^\circ$ . With  $m = 0$ ,  $E_A = 140.9 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $n_3 = 2.5$ ,  $n_5 = 2.84$ . This difference is supportive of a multiple degradative process involving from 10–25 individual reactions.

In multiple  $n^{\text{th}}$  order reactions no clear pattern emerges regarding the variation of  $n_{\text{eff}}$  with  $n_{\text{ind}}$ . As shown in Fig. 2, the variation depends upon the number of members in the set, the manner in which the relative spacing between the individual member extent of reaction—temperature curves changes, and in the case of skewed distributions, the magnitude of the changes. The most interesting multiple sets are those in which the individual members have  $n_{\text{ind}} < 1$ . The effective order of the overall reaction resulting from linear combinations of such low order single reactions, with decremental changes in their relative  $1 - \alpha$  vs.  $T$  curve spacing, can vary from  $\sim 0.5$  to  $\sim 2.3$  [see Figs 2 a1 and 2 a2]. However, if the relative spacing changes incrementally, the overall reaction order varies only from  $\sim 0.5$  to  $\sim 1.5$ .

The second fact emerging from this study, confirms the finding of the previous analytical investigation of multiple first order reactions [5], namely, that the Friedman analysis can result in reaction kinetics parameters,  $E_F$  and  $A_F$  which vary with the extent of the overall reaction. This is the second criterion of a multiple reaction system.

With the exception of the 30D model, for all multiple sets with  $n_{\text{ind}} < 1$ ,  $E_F$  decreases linearly with extent of reaction, according to Eq. (10), up to  $\alpha_{\text{eff}} \sim 0.6$ . The magnitude of  $k_3$  and  $k_4$  are, as demonstrated in Figs 5a and 5b, and Tables 3 and 4, model dependent. With increase in  $n_{\text{ind}}$ ,  $k_4$  becomes increasingly positive. Summarizing the Table 3 data,  $k_4$  decreases as the number of members in the set increases, but increases as the model  $1 - \alpha$  vs.  $T$  relative spacing changes from decremental to incremental. The constant term,  $k_3$ , increases only very slightly with increase in the number of members in the set, and their individual reaction orders, but decreases as the model  $1 - \alpha$  vs.  $T$  relative curve spacing reverts from decremental to incremental.

The most significant changes of the Friedman-derived kinetics parameters with extent of the overall reaction are for the 30D models. In all cases,  $E_F$  increases monotonically with  $\alpha_{\text{eff}}$  which substantiates the findings of the analyses of multiple first order reactions with decremental spacing between contiguous  $1 - \alpha$  vs.  $T$  curves [5].

Turning now to a consideration of experimental thermoanalytical reaction

progress measurements, and their interpretation; the advantages of employing non-isothermal means of investigation, at least in the initial stage of study, cannot be over-emphasized. Although for singular processes, the characteristic shapes of TG-, DTG- and DSC-T curves, from which extents and rates of reaction are calculated, assist in the identification of possible reaction mechanisms, such may not be the case for multiple reactions. One may, perforce, have to analyse data according to an  $n^{\text{th}}$  order mechanism. As has been shown, non-isothermal rising temperature methods of investigation enable an estimation of effective reaction orders. The variation of Friedman-evaluated reaction kinetics parametric data with extent of the overall reaction allows one to assess the potential complexity of the process studied in terms of the contributing single reactions, both number and type. Parameters, evaluated by Kissinger analysis of the same experimental data monitored at several different heating rates, can assist in this interpretation.

However, an  $n^{\text{th}}$  order data analysis is only the first stage. One needs to know what type of overall reaction results from a set of multiple solid state reactions, in which specific rate-controlling mechanisms are at work. This question will be addressed in forthcoming multiple reaction scheme analyses.

\* \* \*

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**Zusammenfassung** — Es wurde eine Analyse der Kinetik von Effektivreaktionen durchgeführt, die sich unter Annahme simulierter nicht-isothermischer Bedingungen mit einem Multipel von unterschiedlich gewählten Aktivierungsenergien und präexponentiellen Faktoren aus der Linearkombination von Einzelreaktionen mit einem breiten Bereich der Reaktionsordnung  $n$  ergaben. Die globalen kinetischen Parameter der einzelnen Modelle wurden unter Anwendung der isokonversiven Friedman-, der Arrhenius- und Kissingeranalysen aus Größe und Quotient der Reaktionsdaten ermittelt, die für eine Anzahl verschiedener Aufheizgeschwindigkeiten generiert wurden. Multiple mit fünf bis fünfzig Elementen mit Werten zwischen 0,25 und 5 wurden betrachtet. Es wird die Abhängigkeit der kinetischen Reaktionsbruttoparameter von der Gestaltung des Modelles besprochen. Es werden Kriterien gegeben,

die an experimentellen thermoanalytischen Daten zur Erkennung von Mehrfachreaktionen angewendet werden können.

**Резюме** — Проведен анализ кинетики эффективных реакций, составленных из линейных комбинаций многочисленных единичных реакций с  $n$ -порядком в широком интервале и взятых с различными энергиями активации и предэкспоненциальными множителями, полученными в модельных неизотермических условиях. Глобальные кинетические параметры некоторых моделей получены обработкой с помощью изоконверсионного анализа Аррениуса, Киссинджера и Фридмана данных о степени и скорости реакций, найденных при разных линейных скоростях нагрева. Учитывались многочисленные наборы, содержащие от 5 до 50 отдельных членов с порядком реакции, изменяющимся от 0,25 до 5. Обсуждено влияние выбранной модели на кинетические параметры перекрывающихся реакций. Представлены критерии, применяемые к экспериментальным термоаналитическим данным для опознания многоступенчатых реакций.