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The 'E–ln(A)–f(α)' triplet in non-isothermal reaction kinetics analysis[1,2]

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Abstract

In determining the kinetics of thermally stimulated solid-state transformations by non-isothermal techniques, there is, as yet, one unsurmountable barrier to establishing separate values of E, A, and f(α). By employing logarithmic plots of various expressions; reaction rate at one heating rate, β, i.e. Arrhenius analysis, isoconversional reaction rates at several heating rates, i.e. Friedman analysis, one easily obtains the value of E, from the plot slope. However, the plot intercept is the logarithm of the product of A and f(α), and over the entire extent of a singular reaction should mirror the behavior of the f(α) parameter defining the mechanism. In examining experimental non-isothermal data, either DSC or TG, obtained by either procedure, this behavioral pattern should assist in identifying the probable reaction mechanism. Rate and extent of reaction data for singular model systems, generated over a wide range of E_{in}, A_{in}, and β for seven f(α) mechanisms, have been employed as vehicles for isoconversional Friedman analysis in an attempt to verify the several model-dependent paradigms in the E_{F}–ln(A_{F})–f(α) relationships over the $0.01\leq\alpha\leq0.99$ range. Isoconversational data resulting from analyses of simulated single solid-state reactions have also been employed to test the utility of proposed 'Kissinger-type' relationships for so-called 'model-free' kinetics. The isoconversional procedure has also been employed to investigate the behavioral patterns observed in the analyses of the three steps in a thermogravimetric study of the degradation of calcium oxalate monohydrate. © 1998 Elsevier Science B.V.

1. Theoretical considerations

Eq. (1a) represents the generally accepted logarithmic expression for the rate of a non-isothermally stimulated solid-state reaction at a set extent of reaction, α, at a temperature, T_α [1].

$$\ln(\mathrm{d}\alpha/\mathrm{d}t)_\alpha = \ln[A_\alpha \times T_\alpha^m \times \mathrm{f}(\alpha)] - E_\alpha/RT_\alpha \tag{1a}$$

where f(α) is the analytical function of the reaction extent, α, descriptive of the reaction mechanism. E_α and A_α are the so-called energy of activation and pre-exponential factor, respectively, and R is the general gas constant. In light of the remarks of Dollimore and Reading [2], it is considered reasonable to use the m=0 approximation. This approach has been followed in this study.

$$\ln(\mathrm{d}\alpha/\mathrm{d}t)_\alpha = \ln[A_\alpha \times \mathrm{f}(\alpha)] - E_\alpha/RT_\alpha \tag{1b}$$

Although recently heavily criticized by Zsako [3], the isoconversional procedure is highly popular. In this method, a set of actual or model-simulated experiments are performed at different linear heating rates. The rates and temperatures of reaction at a pre-defined extent of reaction are measured, and fitted to Eq. (1b).

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[2] Presented at the 25th NATAS Conference, McLean VA. September 1997

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The major premise underlying the use of the isoconversional method is that one is dealing with a single effective reaction with α-invariant kinetics parameters, E_α and A_α, over the entire extent of reaction range, $0 \leq \alpha \leq 1$. Although it is possible to generate ($d\alpha/dt$, T_α) data sets for a simulated single reaction, which will yield a linear Eq. (1b) plot, it is highly unlikely that, in reality, experimentally measured data characterize a single reaction. Budrugeac et al. [4] have recently discussed some of the problems inherent in the application of the isoconversional technique.

In the early stages of the development of this analytical procedure, Friedman [5] employed the *n*th order model (2) to represent $f(\alpha)$.

$$f(\alpha) = (1-\alpha)^n \tag{2}$$

It has been demonstrated [6] that extent (α) and rate ($d\alpha/dt$) of reaction data for various solid-state models can be analyzed using this empirical model. The resulting α–T and $d\alpha/dt$–T data for both the actual and the *n*th order equivalent model are identical. Furthermore, despite large discrepancies in the magnitude of the actual solid-state model kinetics (E, A) parameters compared with the *n*th order equivalent values (E_n, A_n), extents of reaction as a function of temperature at any heating rate are superimposable with those generated using isoconversionally determined parameters with model-corrected pre-exponential factors [7].

Table 1
Solid-state reaction kinetics model parameters, $f(\alpha)$ and $g(\alpha)$

Model	$f(\alpha)$	$g(\alpha)$[a]
*n*th order	$(1-\alpha)^n$	$[1-(1-\alpha)^{1-n}]/(1-n)$
An (n=2 or 3)	$n(1-\alpha)\times[-\ln(1-\alpha)]^{1-1/n}$	$[-\ln(1-\alpha)]^{1/n}$
Rn (n=2 or 3)	$n(1-\alpha)^{1-1/n}$	$1-(1-\alpha)^{1/n}$
D2	$-1/[\ln(1-\alpha)]$	$(1-\alpha)\times\ln(1-\alpha)+\alpha$
D3	$[(3/2)\times(1-\alpha)^{2/3}]/[1-(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$
D4	$[(3/2)\times(1-\alpha)^{1/3}]/[1-(1-\alpha)^{1/3}]$	$1-(2\alpha/3)-(1-\alpha)^{2/3}$

[a] $g(\alpha)=\int d\alpha/f(\alpha)$.

Table 2
ln [$f(\alpha)$] for seven solid-state reaction kinetics models

α	A2	A3	R2	R3	D2	D3	D4
0.05	−0.8432	−0.9328	0.6675	1.0644	2.9702	4.4486	4.4657
0.10	−0.5374	−0.5070	0.6405	1.0284	2.2504	3.7017	3.7368
0.15	−0.3779	−0.2752	0.6119	0.9903	1.8170	3.2397	3.2938
0.20	−0.2800	−0.1245	0.5816	0.9498	1.4999	2.8922	2.9666
0.25	−0.2175	−0.0197	0.5493	0.9068	1.2459	2.6058	2.7016
0.30	−0.1790	0.0547	0.5148	0.8608	1.0309	2.3561	2.4750
0.35	−0.1587	0.1064	0.4778	0.8114	0.8422	2.1300	2.2736
0.40	−0.1535	0.1400	0.4377	0.7581	0.6717	1.9192	2.0895
0.45	−0.1619	0.1578	0.3942	0.7001	0.5144	1.7179	1.9172
0.50	−0.1833	0.1611	0.3466	0.6365	0.3665	1.5218	1.7528
0.55	−0.2179	0.1501	0.2936	0.5663	0.2250	1.3296	1.5931
0.60	−0.2669	0.1240	0.2350	0.4878	0.0874	1.1295	1.4349
0.65	−0.3324	0.0812	0.1682	0.3987	−0.0486	0.9254	1.2754
0.70	−0.4180	0.0184	0.0912	0.2960	−0.1856	0.7098	1.1111
0.75	−0.5298	−0.0699	0.0000	0.1744	−0.3266	0.4754	0.9375
0.80	−0.6783	−0.1936	−0.1116	0.0257	−0.4759	0.2115	0.7480
0.85	−0.8838	−0.3716	−0.2554	−0.1661	−0.6403	−0.1014	0.5309
0.90	−1.1924	−0.6480	−0.4581	−0.4364	−0.8340	−0.5057	0.2619
0.95	−1.7540	−1.1657	−0.8047	−0.8985	−1.0972	−1.1322	−0.1336

Irrespective of the isoconversional procedure employed, either the differential or integral (vide infra) approach, the activation energy of the assumed single reaction is obtained from the slope of the logarithmic plots, Eq. (1b) in the differential method, at various degrees of conversion. However, one cannot calculate the pre-exponential factor without a knowledge of the f(α) function, which, as will be shown, varies significantly and differently with α for all solid-state models. Budrugeac et al. [4] have discussed their views regarding how the investigator should proceed by suggesting criteria for establishing correct f(α) functions when dealing with actual experimental data. Furthermore, they indicate their preference for using

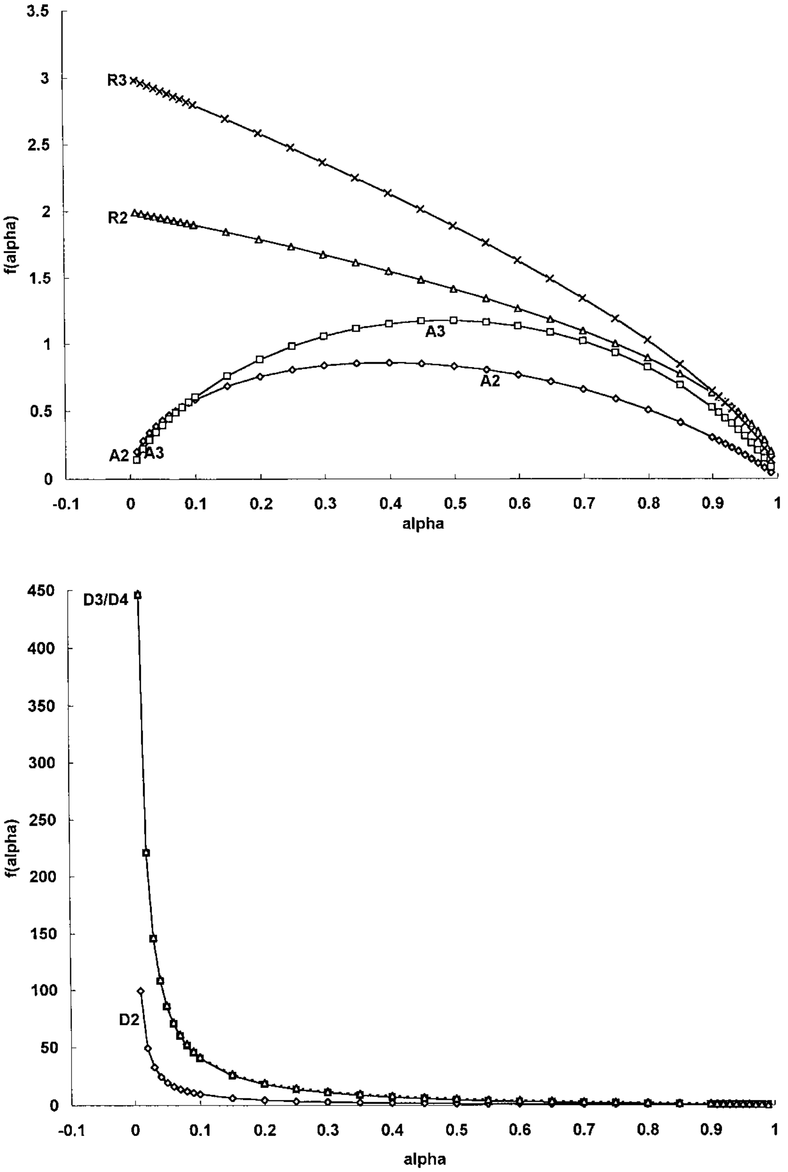

Fig. 1. (a) f(α) as a function of α for the solid-state models A2, A3, R2, and R3. (b) f(α) as a function of α for the solid-state models D2, D3, and D4.

the differential rather than the integral approach, if one wishes to test quickly for constant E_α. Zsako [3], who employs the empirical *n*th order model, Eq. (2), and, it appears, the integral approach, observes that much of the experimental data employed in support of his critique, show a systematic decrease in both calculated E_α and A_α, and an increase in the reaction order, '*n*', with increasing heating rate. Furthermore, it is stated that in performing model analyses, more realistic TG data, exhibiting such heating rate-dependent characteristics should be employed in investigating the utility of the 'many curves' method. It is considered that such a selection protocol defeats the purpose of establishing the correctness of the isoconversional procedure. One should not be too surprised at his conclusions.

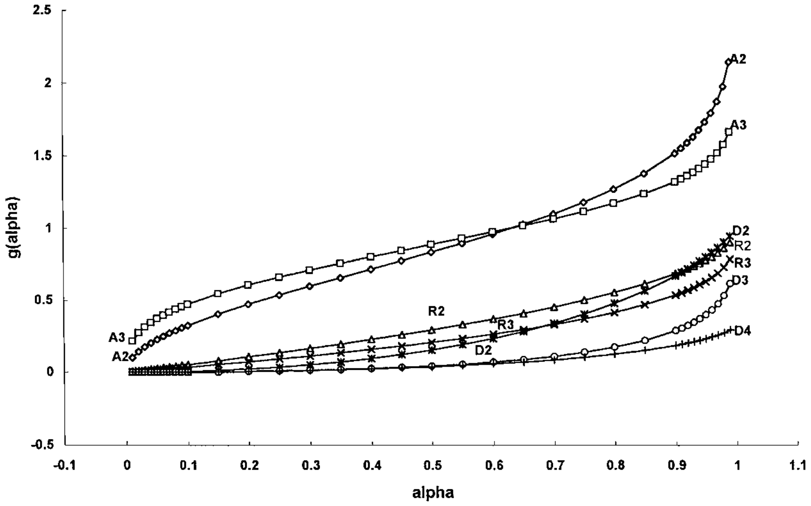

Fig. 2. g(α) as a function of α for the solid-state models A2, A3, R2, R3, D2, D3, and D4.

Table 3
ln [g(α)] for seven solid-state reaction kinetics models

α	A2	A3	R2	R3	D2	D3	D4
0.05	−1.4851	−0.9901	−3.6761	−4.0773	−6.6677	−8.1547	−8.1661
0.10	−1.1252	−0.7501	−2.9697	−3.3665	−5.2638	−6.7330	−6.7563
0.15	−0.9085	−0.6057	−2.5505	−2.9425	−4.4347	−5.8851	−5.9209
0.20	−0.7500	−0.5000	−2.2484	−2.6355	−3.8404	−5.2710	−5.3200
0.25	−0.6229	−0.4153	−2.0101	−2.3921	−3.3744	−4.7842	−4.8470
0.30	−0.5155	−0.3436	−1.8119	−2.1884	−2.9892	−4.3768	−4.4545
0.35	−0.4211	−0.2807	−1.6411	−2.0117	−2.6594	−4.0234	−4.1168
0.40	−0.3359	−0.2239	−1.4899	−1.8543	−2.3697	−3.7085	−3.8188
0.45	−0.2572	−0.1715	−1.3533	−1.7110	−2.1104	−3.4221	−3.5504
0.50	−0.1833	−0.1222	−1.2279	−1.5784	−1.8745	−3.1569	−3.3048
0.55	−0.1125	−0.0750	−1.1112	−1.4538	−1.6572	−2.9075	−3.0769
0.60	−0.0437	−0.0291	−1.0009	−1.3349	−1.4546	−2.6697	−2.8627
0.65	0.0243	0.0162	−0.8955	−1.2199	−1.2639	−2.4397	−2.6589
0.70	0.0928	0.0619	−0.7935	−1.1069	−1.0823	−2.2139	−2.4628
0.75	0.1633	0.1089	−0.6931	−0.9941	−0.9078	−1.9883	−2.2716
0.80	0.2379	0.1586	−0.5928	−0.8790	−0.7379	−1.7580	−2.0821
0.85	0.3202	0.2134	−0.4899	−0.7579	−0.5702	−1.5157	−1.8903
0.90	0.4170	0.2780	−0.3801	−0.6239	−0.4009	−1.2478	−1.6898
0.95	0.5486	0.3657	−0.2531	−0.4595	−0.2229	−0.9190	−1.4656

For single reactions with α-invariant kinetics parameters, the intercepts of the Eq. (1b) plots should mirror the behavioral pattern of the f(α) mechanistic functions over the entire α-range. It is the purpose of this investigation to verify this fact by describing the findings of a set of isoconversional calculations of simulated singular non-isothermal reactions conforming to seven solid-state models A2, A3, R2, R3, D2, D3 and D4 [8]. A wide range of constant E and A input parameters was used to generate extent and rate of reaction–temperature data at several linear heating rates from 1 to 100°C/min. Friedman isoconversional analyses were performed using a general purpose fortran program, KINMOD1, previously employed by the author to investigate several mutually independent multiple reaction systems [9]. All calculations used the m=0 temperature exponent approximation. The original program has been modified by employing

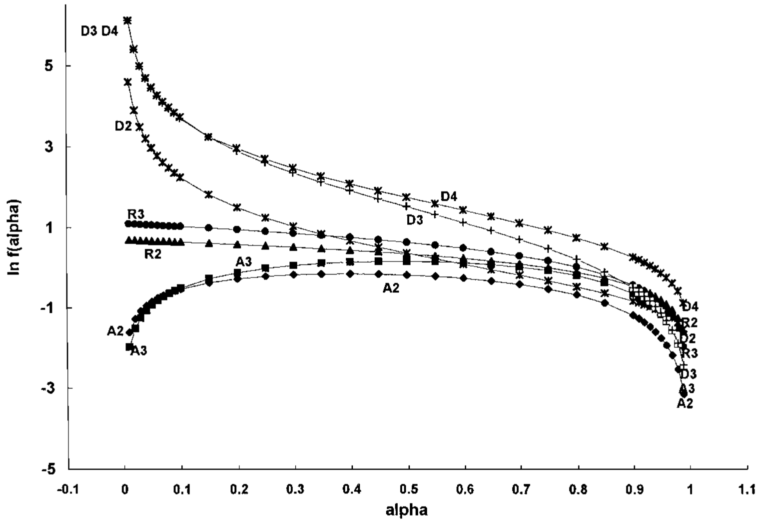

Fig. 3. ln[f(α)] as a function of α for the solid-state models A2, A3, R2, R3, D2, D3, and D4.

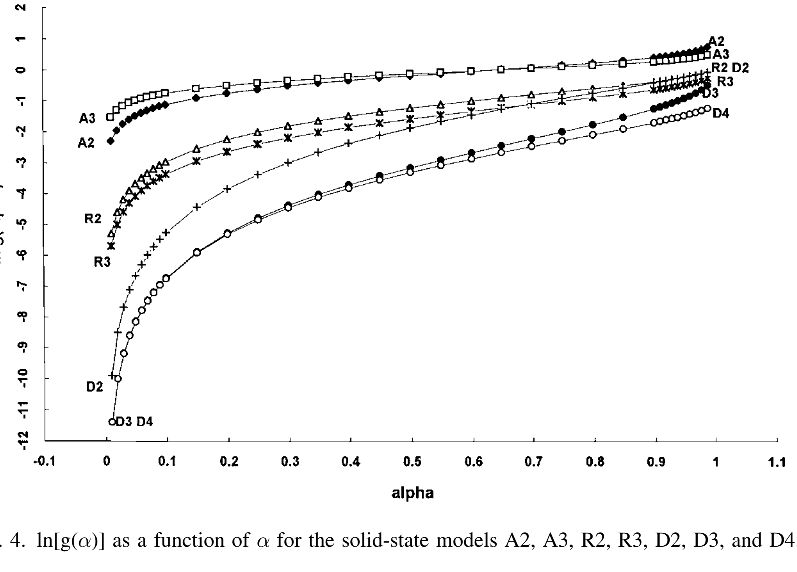

Fig. 4. ln[g(α)] as a function of α for the solid-state models A2, A3, R2, R3, D2, D3, and D4.

the fourth degree rational approximation of Senum and Yang [10] to compute the p(*E*/*RT*) function used to calculate the f(α) and the inverse integral function g(α) employed at various stages in the data analyses. Recently, integral procedures have been described which purport to generate reaction kinetics parameters without specifying the f(α) functional model, the so-called 'model-free' kinetics [11], utilizing Vyazovkin's 'Kissinger-like' Eq. (3).

$$\ln\{[\beta/(T_\alpha)^2\} = \ln\{[A_\alpha \times R]/[E_\alpha \times \mathrm{g}(\alpha)]\} - E_\alpha/RT_\alpha \qquad (3)$$

It appears that Vyazovkin employs the first two terms of the polynomial expression for the temperature integral p(*E*/*RT*) function [1,12] in developing this equation for *E*/2*RT*>>1. It is expected that the isoconversional logarithmic intercept of this equation will vary with α in a manner similar to that expected for the comparable intercept in the more simple Eq. (1b). Calculations have been carried out in an attempt to verify this expectation.

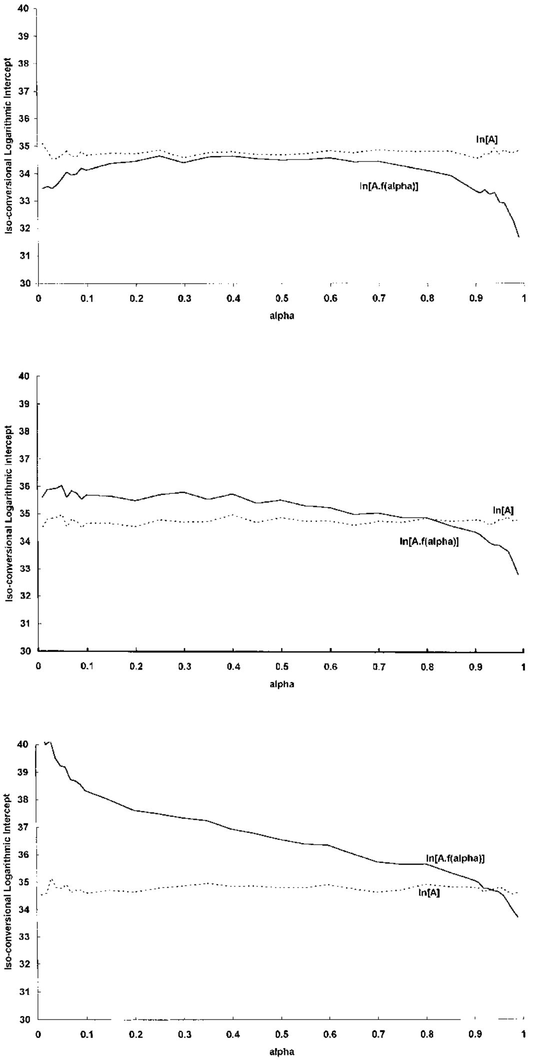

Fig. 5. (a) Eq. (1b) isoconversional logarithmic intercepts as a function of α for the A2 solid-state model with input parameters, E=220 kJ/mol and A=1.25×10^{15} min^{-1}. (b) Eq. (1b) isoconversional logarithmic intercepts as a function of α for the R3 solid-state model with input parameters, E=220 kJ/mol and A=1.25×10^{15} min^{-1}. (c) Eq. (1b) isoconversional logarithmic intercepts as a function of α for the D4 solid-state model with input parameters, E=220 kJ/mol and A=1.25×10^{15} min^{-1}.

2. Model calculations

Table 1 lists the f(α) and g(α) i.e. [$\int$dα/f(α)] functions for seven solid-state models [2]. Fig. 1(a) and (b), and Fig. 2, show the f(α) and g(α) functions, respectively, over the complete α-range. The differences in the α-dependencies of the several f(α) and g(α) functions are immediately obvious. Tables 2 and Table 3 list ln[f(α)] and ln[g(α)] as functions of α for these seven models, and Figs. 3 and 4 show the dependencies. With E_{in}=220 kJ/mol and A_{in}=1.25×10^{15} min^{-1} as input parameters, $\alpha-T$ and dα/d$t-T$ curves were generated, and from the Friedman isoconversional analyses, E_{F} and A_{F} values computed. Fig. 5(a–c) show the logarithmic intercepts as functions of α for the A2, R3 and D4 solid-state models. As can be seen, they almost exactly mirror the ln[f(α)] variations depicted in Fig. 3 for these models. The results are summarised in Table 4. As can be seen, the activation energies are essentially constant at $\geq$99.9% of the correct value. Similarly, the logarithms of the pre-exponential factors are constant at $\geq$99.9% of the correct value. Similar results were obtained with other input parameters. It is proposed that in dealing with experimental multi-heating rate TG/DSC data, one should use the characteristic α-dependency of the intercept of the logarithmic isoconversional plot to establish by pattern recognition the probable f(α) mechanistic parameter. If this is inconclusive, and

Table 4
Isoconversional E_F and In (A_F) values. E_{in}=220 kJ/mol, $A_{in}=1.25\times10^{15}$ min^{-1}, ln(A_{in})=34.7619

Model	E_F (kJ/mol)		ln(A_F)	
	Mean value	σ	Mean value	σ
A2	219.7	0.57	34.735	0.091
A3	219.8	0.55	34.753	0.086
R2	219.7	0.60	34.739	0.100
R3	219.7	0.59	34.739	0.099
D2	219.7	0.59	34.728	0.109
D3	219.6	0.65	34.727	0.113
D4	219.6	0.65	34.726	0.114

furthermore, if E_α is not constant, then one is probably dealing with either a change in mechanism as the reaction proceeds or a more compex situation such as a mutually independent multiple, competitive or consecutive reaction system. Using these isoconversionally derived parameters, the logarithmic intercepts of the integral Eq. (3) were calculated and are listed in Table 5 for the several models and displayed in Fig. 6. As is seen, there is noticeable curvature at ca. $\alpha\leq0.1$ dependent upon the model. In general, as shown in Table 6, there is an approximate linear relationship between the logarithmic intercept and α.

Table 6
Summary of 'model-free kinetics' equation $\ln\{[A_\alpha\times R]/[E_\alpha\times g(\alpha)]\}=K_1+K_2\times\alpha$

Model	α-range	# of pairs	K_1	K_2	r^2
A2	0.05–0.95	19	25.7264	−1.8387	0.9686
A3	0.05–0.95	19	25.3806	−1.3098	0.9608
R2	0.05–0.95	19	27.5032	−3.0338	0.9510
R3	0.05–0.95	19	27.9478	−3.2670	0.9376
D2	0.05–0.95	19	29.8017	−5.8799	0.9519
D3	0.05–0.95	19	31.3600	−6.5453	0.9594
D4	0.05–0.95	19	31.3385	−6.0672	0.9582

3. Experimental data calculations

The application of the isoconversional analysis procedure to the three steps in the sequential degradation of calcium oxalate monohydrate, thermogravimetrically is presented [6]. The experimental TG data, previously described, are shown in Fig. 7. Table 7 summarizes the data at $\Delta\alpha$ intervals from 0.05 to 0.95. As previously indicated [6], the input data were obtained by fitting the experimental TG data as a function of temperature, monitored over a 100% change in heating rates, to an *n*th order model using the instrumental system software. In agreement with

Table 5
$\ln\{[A_\alpha\times R]/E_\alpha\times g(\alpha)]\}$ values for seven solid-state kinetics models [11]

α	A2	A3	R2	R3	D2	D3	D4
0.05	25.9608	25.4736	28.2671	28.8582	31.1269	32.6406	32.6597
0.10	25.6055	25.2844	27.3851	27.8442	29.6441	31.3358	31.1359
0.15	25.4672	25.2558	26.9502	27.4116	28.9133	30.4076	30.4274
0.20	25.2845	25.2020	26.6930	26.9880	28.5790	29.7065	29.7728
0.25	25.2897	24.9118	26.6297	26.9936	27.9320	29.3407	29.4327
0.30	24.9009	24.9236	26.1835	26.7012	27.5968	28.8091	29.1225
0.35	24.9918	24.8451	26.2917	26.1752	27.2199	28.6861	28.8801
0.40	24.9347	24.8297	26.0612	26.6346	27.0618	28.0836	28.4620
0.45	24.7649	24.6474	26.0358	26.2153	26.5347	27.8170	28.2007
0.50	24.6705	24.8121	25.8348	26.2637	26.4254	27.6901	27.9047
0.55	24.6440	24.6118	25.7605	26.0082	26.2652	27.4833	27.6743
0.60	24.6814	24.4433	25.5517	25.8953	25.8683	27.4065	27.5670
0.65	24.5386	24.4113	25.4978	25.6321	25.8927	26.9945	27.2163
0.70	24.5709	24.4308	25.2817	25.6660	25.6911	26.7588	26.8973
0.75	24.4465	24.6117	25.3033	25.5162	25.4607	26.7267	26.7862
0.80	24.3657	24.4383	25.0955	25.5417	25.3360	26.3046	26.7942
0.85	24.2965	24.2917	25.0282	25.3208	25.0680	26.1178	26.5164
0.90	23.9632	24.1508	25.0223	25.2330	25.1149	25.7724	26.2899
0.95	23.9570	24.2128	24.8662	25.0735	24.6436	25.5784	26.0534

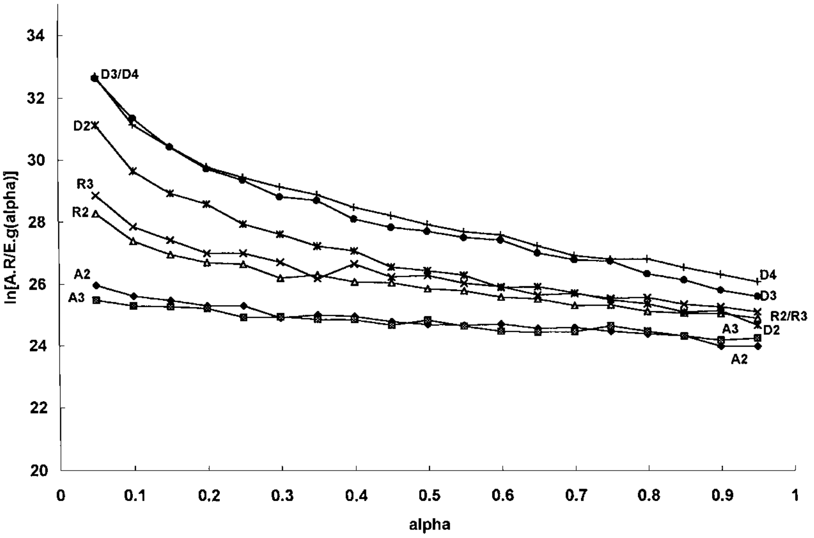

Fig. 6. Eq. (3) isoconversional logarithmic intercepts as a function of α for the solid-state model A2, A3, R2, R3, D2, D3, and D4 with input parameters, E=220 kJ/mol and A=1.25×10^{15} min^{-1}.

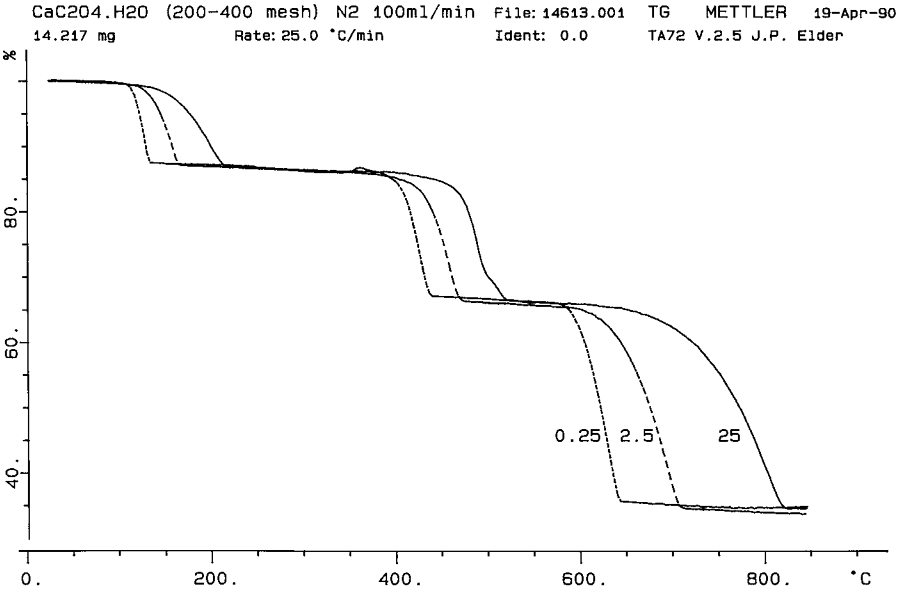

Fig. 7. Experimental non-isothermal TG curves of the three steps in the thermal degradation of calcium oxalate monohydrate at three heating rates, 0.25, 2.5 and 25°C/min.

Zsako [3], the parameters E_n and $\ln(A_n)$ decreased with increase in the heating rate but the reaction order, n, remained relatively constant. Since no assumption was made as to the reaction mechanism of each step in generating the input parameter set, $[E_n, \ln(A_n), n]$, it is considered to be in order in this application to use such empirically generated extent and rate of reaction figures since it has been shown that, after sample weight normalization, they were essentially superimposable on the original weight change curves. For each

Table 7
Friedman analyses: Calcium oxalate monohydrate three-step degradation [6]

α	Step 1	–H_2O	$r^2 \geq 0.989$	Step 2	–CO	$r^2 \geq 0.998$	Step 3	–CO_2	$r^2 \geq 0.998$
			Model D4		Model R3			Model D4	
	E_α (kJ/mol)	$\ln[A_\alpha \times f(\alpha)]$	$A_\alpha \times 10^{-7}$ (min^{-1})	E_α (kJ/mol)	$\ln[A_\alpha \times f(\alpha)]$	$A_\alpha \times 10^{-17}$ (min^{-1})	E_α (kJ/mol)	$\ln[A_\alpha \times f(\alpha)]$	$A_\alpha \times 10^{-8}$ (min^{-1})
0.05	99.3	26.600	410.030	256.4	39.439	0.463	229.3	25.417	12.557
0.10	92.5	24.310	86.043	258.1	39.793	0.684	218.7	24.012	6.386
0.15	89.3	23.524	46.632	259.5	40.042	0.911	211.9	23.120	4.078
0.20	86.7	22.043	27.622	263.1	40.630	1.710	208.1	22.641	3.504
0.25	84.2	21.620	16.442	261.8	40.408	1.429	204.6	22.192	2.914
0.30	82.0	20.916	10.205	265.3	40.960	2.599	201.7	21.817	2.513
0.35	81.3	20.672	9.782	262.8	40.509	1.740	199.3	21.494	2.226
0.40	80.1	20.308	8.172	264.1	40.686	2.190	196.6	21.150	1.895
0.45	78.6	19.486	6.114	264.9	40.786	2.565	195.5	20.994	1.927
0.50	77.9	19.578	5.514	265.7	40.860	2.943	193.8	20.762	1.800
0.55	77.7	19.475	5.833	267.1	41.021	3.708	192.3	20.556	1.719
0.60	76.0	18.955	4.063	267.5	41.035	4.070	191.3	20.392	1.709
0.65	76.1	18.920	4.604	266.0	40.713	3.223	189.5	20.133	1.547
0.70	74.8	18.487	3.517	266.6	40.712	3.569	188.3	19.934	1.495
0.75	74.2	18.267	3.360	267.7	40.785	4.355	187.0	19.717	1.432
0.80	72.9	17.822	2.600	268.6	40.784	5.023	186.5	19.580	1.510
0.85	72.5	17.601	2.591	267.6	40.437	4.301	184.7	19.269	1.373
0.90	71.8	17.245	2.375	268.7	40.361	5.228	183.8	19.000	1.373
0.95	70.2	16.514	1.699	268.1	39.819	4.825	182.2	18.537	1.284

step, at each of the heating rates, the Friedman plot regression analyses showed excellent correlation coefficients, as indicated at each α. One observes in Fig. 8(a) that, for all three steps, E_α is not constant but changes monotonically with α, implying that one is monitoring an effective but not a singular reaction. The isoconversional logarithmic plot intercepts, shown in Fig. 8(b), indicate that the overall reactions conform best to the models:

Step 1 – loss of water – D4

Step 2 – loss of carbon monoxide – R3

Step 3 – loss of carbon dioxide – D4

as originally proposed, based upon ‘peak analysis-determined’ models [6]. Fig. 8(c) shows the computed logarithms of the pre-exponential factors.

4. Conclusions

- The procedure described should be considered as integral-differential, since its use necessitates integral methods in generating the Friedman data for the isoconversional analysis. Isoconversional analyses of modelled solid-state reactions demonstrate that the intercepts of logarithmic rate equations mirror exactly the characteristic f(α) functions describing the reaction mechanism, confirming the utility of the procedure in assisting the investigator to ascribe a mechanism descriptive of monitored non-isothermally generated thermoanalytical behavior.
- The isoconversional logarithmic intercept of the integral Eq. (3) does exhibit α-variant behavior in a manner similar to that shown for the comparable term in the more simple differential Eq. (1b) investigated in this study.
- Applications of the procedure in the analysis of non-isothermally generated experimental degradative data show that, in spite of the fact that the calculated effective reaction activation energy can vary slightly as the reaction proceeds to conclusion, the logarithmic plot intercept conforms well to realistic f(α) functional behavior.

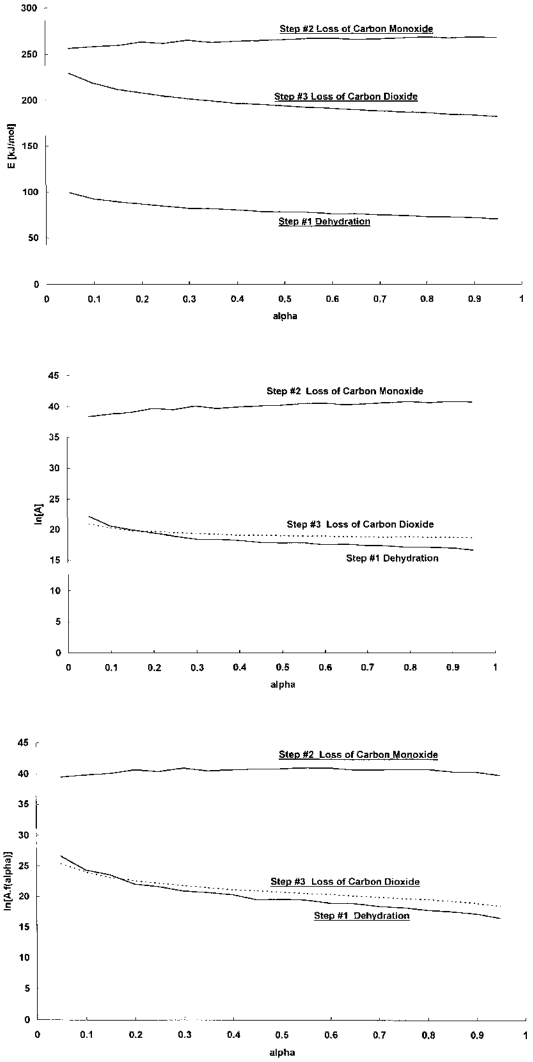

Fig. 8. (a) Isoconversional activation energy-α profiles for the three steps in the thermal degradation of calcium oxalate monohydrate. (b) Isoconversional logarithmic intercept-α profiles for the three steps in the thermal degradation of calcium oxalate monohydrate. (c) Isoconversional logarithm of the pre-exponential factor-α profiles for the three steps in the thermal degradation of calcium oxalate monohydrate.

- The effective first and third stages in the thermal degradation of calcium oxalate monohydrate appear to conform to the three-dimensional diffusion (Ginstling–Brounshtein D4) model, while the second stage appears to conform to the three-dimensional phase boundary movement (R3) model. (See Elder [1] for detailed references.)
- It is considered unnecessary in modelling solid-state degradative reaction systems to employ as input parameters decreasing activation energies pre-exponential factors, and increasing reaction orders, rather than constant values, at different heating rates, as has been proposed [3], and it is considered that there is virtue in the use of the referred-to ‘many curves’ methods.

References

[1] J.P. Elder, in: P.S. Gill, J.F. Johnson (Eds.), Analytical Calorimetry, vol. 5, Plenum Press, New York, 1984, p. 255.
[2] D. Dollimore, M.J. Reading, Treatise on analytical chemistry, in: J.D. Winefordner (Ed.), Thermal Methods, chap. 1, part 1, vol. 13, 2nd ed., Wiley, 1993, p. 37.
[3] J. Zsako, J. Thermal Anal. 46 (1996) 1845.
[4] P. Budrugeac, A.L. Petre, E. Segal, J. Thermal Anal. 47 (1996) 123.
[5] H.L. Friedman, J. Polym. Sci. C6 (1965) 175.
[6] J.P. Elder, Thermochim. Acta 243 (1994) 209.
[7] J.P. Elder, Thermochim. Acta 272 (1996) 41.
[8] M.E. Brown, D. Dollimore, A.K. Galwey, in: C.H. Bamford, C.E.H. Tipper (Eds.), Comprehensive Chemical Kinetics, chap. 3, vol. 22, Elsevier, New York, 1980, p. 90.
[9] J.P. Elder, J. Thermal Anal. 29 (1984) 1327; 34 (1988) 1467; 35 (1989) 1965; 36 (1990) 1077; 39 (1993) 467.
[10] G.I. Senum, R.T. Yang, J. Thermal Anal. 11 (1977) 445.
[11] S. Vyazovkin, Mettler-toledo STAR® system, version 3.1, Operational Manual, sec. 11.9.
[12] J. Sestak, Thermochim. Acta 3 (1971) 150.