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Reconciliation of Arrhenius and iso-conversional analysis kinetics parameters of non-isothermal data[1]

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Abstract

Calculations pertaining to *n*th order analyses of various solid state reaction kinetics models have been extended to consider iso-conversional Arrhenius (i.e. Friedman) analyses. Non-isothermal extent and rate of reaction data for several models, with the same kinetics parameters, generated over a wide heating rate range, are subjected to both Arrhenius and Friedman *n*th order analyses over the entire extent of reaction range. A necessary model correction for the Friedman preexponential factors is presented and discussed. Calculated extent of reaction as a function of temperature data at a desired heating rate is compared with the original model data and analogous data generated using the single heating rate Arrhenius analyses parameters. Essentially complete agreement is obtained despite the widely disparate values of the Arrhenius and Friedman derived kinetics parameters. Application of this procedure to the analysis of experimental data is discussed.

Keywords: Arrhenius; Freidman; Kinetics; Non-isothermal

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1. Introduction

It has been demonstrated that non-isothermal degradative reaction data for all solid state models may be simulated with very high accuracy by the use of the *n*th order Arrhenius rate equation and its integral form [1]. Furthermore, it was shown that the kinetics parameters of the analogous equation for the actual solid state model may be obtained by multiplying the *n*th order parameters by a correction factor. The multiplicative factor for the activation energy (*E*) is specific for each model and essentially constant. Thus, this factor increases from ca. 0.5 and 0.3, respectively, for the Avrani models A2 and A3,

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through ca. 1.0 for the phase boundary movement models R2 and R3, to ca. 2.1 for the two- and three-dimensional diffusion models D2, D3 and D4 [1]. The companion multiplicative corrector for the pre-exponential factor (A) when expressed logarithmically, is essentially constant for the R2 and R3 models at ca. –0.7 and –1.3, respectively. Refer to Table 1 and reference [2] for description of kinetic models. On the other hand, this correcting factor varies linearly with $E/RT_{\max}$ at the maximum reaction rate. For example, for models A2 and D4, $\ln(A/A_n)$ equals $-5.0 - 0.94(E/RT_{\max})$ and $-1.0 + 0.5(E/RT_{\max})$, respectively. The reader is referred to the earlier publication [1] for the exact values of all correction factors for all seven major solid state models. When applied to experimental *n*th order analysed non-isothermal thermogravimetric data characterizing the three-stage degradation of calcium oxalate monohydrate, this "ratio calculation" procedure enables evaluation of the model reaction kinetics parameters within 99.5% of the correct values.

The benefit of employing iso-conversional Arrhenius analysis to determine the reaction kinetics parameters has long been advocated [3,4]. For singular reactions, the energy of activation, determined using the iso-conversional approach, i.e. employing the Friedman equation [5], is independent of both the model employed in the analysis and the extent of reaction at which the calculation is carried out. Furthermore, the activation energy and pre-exponential factor calculated over the entire extent of the reaction are related through a compensation relationship of the form $\ln A = k_1 \cdot E + k_2$, where k_1 and k_2 are constants. The utility of the iso-conversional approach in assessing the possibility of the occurrence of multiple reactions has been emphasized in a series of papers [6]. Earlier, the danger of relying solely on single heating rate data to determine the correct reaction kinetics parameters had been discussed by Elder [3].

It is the purpose of this paper to, in a sense, refute this caveat. It is demonstrated how one can, for singular model reactions, using iso-conversionally determined parameters, generate extent of reaction data identical with that descriptive of the original model, thereby achieving a reconciliation of two apparently different sets of kinetics parameters.

2. Theoretical principles

The rate and extent of a singular solid state reaction is given by the differential Arrhenius equation and its integral form [7] at a specific heating rate, β.

$$d\alpha / dt = A\exp(-E / RT)f(\alpha) \tag{1}$$

$$g(\alpha) = (AE / \beta R)p_0(E / RT) \tag{2}$$

where $f(\alpha)$ = function of extent of reaction,

$$g(\alpha) = \int_0^{\alpha} d\alpha / F(\alpha)$$

and $p_0(E/RT)$ is the exponential temperature integral [7]. The integral $g(\alpha)$ may be ex-

Table 1

Solid state reaction kinetics model parameters, $f(\alpha)$, $g(\alpha)$

Model [2]	$f(\alpha)$ [7]	$g(\alpha)$ [8]
Fn[a]	$(1-\alpha)^n$	$[1-(1-\alpha)^{1-n}]/(1-n)$
An[b]	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$	$[-\ln(1-\alpha)]^{1/n}$
Rn[b]	$n(1-\alpha)^{1-1/n}$	$1-(1-\alpha)^{1/n}$
D2	$-1/\ln(1-\alpha)$	$(1-\alpha)\ln((1-\alpha)+\alpha$
D3	$[(3/2)(1-\alpha)^{2/3}]/[1-(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$
D4	$[(3/2)(1-\alpha)^{1/3}]/[1-(1-\alpha)^{1/3}]$	$1-(2\alpha/3)-(1-\alpha)^{2/3}$

[a] nth order.
[b] $n = 2$ or 3.

pressed solely in terms of the extent of reaction, α [8]. Table 1 lists the $f(\alpha)$ and $g(\alpha)$ functions for various solid state models [2]. Eq. (1) may be expressed in terms of the correct model $f(\alpha)$ function, or the equivalent nth order function. Denoting nth order parameters with the subscript n, one has two equivalent forms of the iso-conversional (Friedman [5]) equation.

$$\ln[(\mathrm{d}\alpha/\mathrm{d}t)_\alpha / f(\alpha)] = \ln A - E/RT_\alpha \tag{3a}$$

$$\ln[(\mathrm{d}\alpha/\mathrm{d}t)_\alpha / f_n(\alpha)] = \ln A_n - E_n/RT_\alpha \tag{3b}$$

Since, as has been indicated and will be demonstrated, $E = E_n$, at any α, the correct pre-exponential factor is given by

$$\ln A = \ln A_n + \ln[f_n(\alpha)/f(\alpha)] \tag{4}$$

The temperature at any particular value of α is given by

$$T_\alpha = E/Rp_0^{-1}(E/RT_\alpha) \tag{5}$$

where $p_0^{-1}(E/RT)$ is the inverse $p_0(E/RT)$ function. The third order polynomial generalized form of the Doyle equation, introduced in 1984 [7], is used to calculate the inverse function. $p_0(E/RT_\alpha)$ is obtained by equating the right-hand side of Eq. (2) with the appropriate $g(\alpha)$ function given in Table 1.

3. Simulated solid state reactions

The extent and rate of reaction data as a function of temperature have been generated at various heating rates for the seven solid state models indicated in Table 1 with, in each case, $E = 220$ kJ mol^{-1} and $A = 1.25 \times 10^{15}$ min^{-1}. For each model, the entire data set was subjected to nth order single heating rate analysis, multi-heating rate peak (gener

Table 2

Model A3 $E = 220$ kJ mol^{-1}, $A = 1.25 \times 10^{15}$ min^{-1}, *Fn* analysis

$1-\alpha$	1.00°C min^{-1} Arrhenius: *Fn* ($n = 0.985$)			Kissinger: *Fn* ($n = 0.928$)			Friedman (iso-conversional) input data			*An* ($n = 3.000$) corrected data	
	E/(kJ mol^{-1})	ln(*A*)	Temp./°C	*E*/(kJ mol^{-1})	ln(*A*)	Temp./°C	*E*/(kJ mol^{-1})	ln(*A*)	Temp./°C	ln(*A*)	Temp./°C
0.99	680.43	114.6100	403.7	219.85	34.6930	357.1	219.27	32.6950	385.4	34.6639	403.1
0.98			407.6			367.2	220.68	33.3910	389.5	34.8951	407.3
0.97			409.9			373.4	220.50	33.6370	391.6	34.8682	409.5
0.96			411.5			377.8	219.76	33.7200	392.8	34.7567	410.8
0.95			412.8			381.3	218.93	33.7270	393.9	34.6122	412.0
0.94			413.8			384.2	219.52	33.9380	395.2	34.6989	413.4
0.93			414.8			386.7	220.78	34.2570	396.4	34.9124	414.5
0.92			415.5			388.9	220.89	34.3710	397.1	34.9346	415.2
0.91			416.2			390.8	218.70	34.0860	397.2	34.5683	415.5
0.90			416.9			392.6	219.86	34.3430	398.3	34.7522	416.5
0.89			417.5			394.2	220.53	34.5240	399.0	34.8668	417.2
0.88			418.0			395.7	219.85	34.4750	399.2	34.7569	417.5
0.87			418.5			397.1	221.06	34.7370	400.0	34.9627	418.2
0.86			418.9			398.4	219.51	34.5230	400.1	34.6963	418.5
0.85			419.4			399.6	219.71	34.6120	400.5	34.7364	418.8
0.84			419.8			400.7	220.18	34.7290	401.1	34.8074	419.4
0.83			420.1			401.8	219.78	34.7190	401.2	34.7540	419.5
0.82			420.5			402.8	218.53	34.5530	401.2	34.5468	419.6
0.81			420.9			403.8	221.23	35.0300	402.4	34.9847	420.7
0.80			421.2			404.7	218.72	34.6640	401.8	34.5814	420.3
0.79			421.5			405.6	218.81	34.7080	402.3	34.5898	420.7
0.78			421.8			406.5	219. 34	34.8350	402.6	34.6826	421.1
0.77			422.1			407.3	219.90	34.9580	403.1	34.7728	421.5
0.76			422.4			408.2	219.91	34.9830	403.5	34.7662	421.9
0.75			422.7			408.9	220.90	35.1890	403.9	34.9417	422.2

alized Kissinger) and iso-conversional (Friedman) analyses, as has been described [3]. The Arrhenius, Kissinger and Friedman kinetics parameters were then employed to generate the temperatures, T_α, for various extents of reaction, α, using Eq. (5). The *n*th order iso-conversional pre-exponential factors were corrected for the particular model according to Eq. (4).

Table 2 shows part of a typical set of such data for the three-dimensional random nucleation model, A3, at 1°C min^{-1}, for the range $0.99 \leq 1-\alpha \leq 0.75$. As can be seen, the iso-conversional activation energies are essentially constant. Over the entire α-range, $E_F = 219.93 \pm 0.81$ kJ mol^{-1}. This mean value is in excellent agreement with that derived from Kissinger "peak" analyses, $E_K = 219.85$ kJ mol^{-1}. Even though both were generated using the *n*th order model, they agree with the activation energy of the original solid state model. Using the model-corrected iso-conversional pre-exponential factor one finds over the entire α-range, $\ln A_F = 0.1630E_F - 1.0625$ ($r^2 = 0.9989$). As can be seen, the temperatures computed using the Kissinger kinetics parameters lag the Arrhenius analysis values considerably. This lag is lessened when the temperatures are computed using the *n*th order iso-conversional parameters. However as indicated, the temperature difference can be as much as 20°C. On the other hand, when the model-corrected iso-conversional pre-exponential factors are used with the essentially constant Friedman activation energy, the lag is reduced to an average value <0.5°C.

Figs. 1–3 show for comparison the non-isothermal $1-\alpha$ versus T curves for three solid state models: two-dimensional random nucleation, A2; three-dimensional phase boundary movement, R3; and the Ginstling–Brounshtein model of three-dimensional diffusion, D4, with $E = 220$ kJ mol^{-1} and $A = 1.25 \times 10^{15}$ min^{-1}, at 1°C min^{-1}. Up to 10% deviation from linearity was allowed in computing the equivalent *n*th order Arrhenius parameters, which are as indicated. The circles indicate the T_α values at $\Delta\alpha = 0.05$ increments over the range, $0.05 \leq \alpha \leq 0.95$, computed using these parameters. As previously indicated [1], the agreement with the actual model values is excellent.

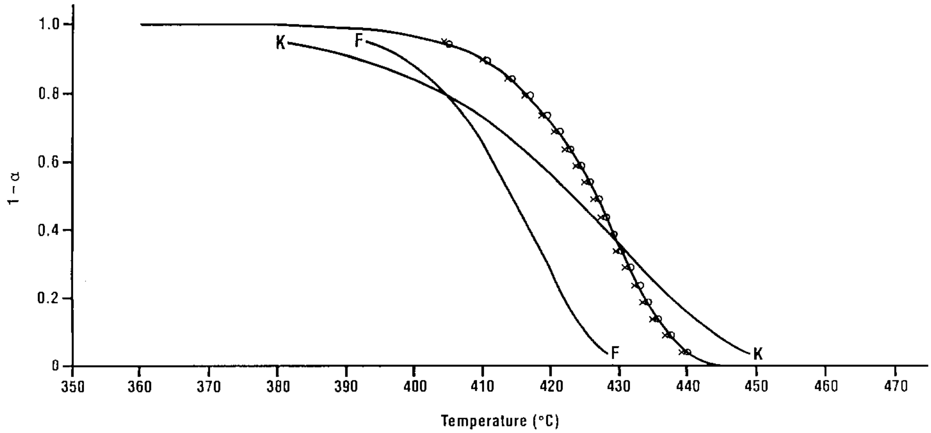

Fig. 1. Model A2: $E = 220$ kJ mol^{-1}, $A = 1.25 \times 10^{15}$ min^{-1}, $\beta = 1$°C min^{-1}. *n*th order analyses: $n = 0.987$, $E_n = 449.7$ kJ mol^{-1}, $A_n = 2.84 \times 10^{32}$ min^{-1}.

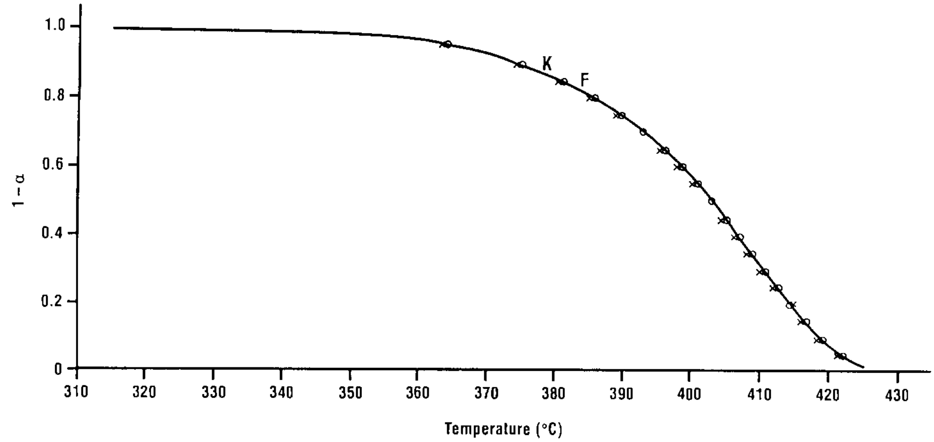

Fig. 2. Model R3: $E = 220$ kJ $\mathrm{mol^{-1}}$, $A = 1.25 \times 10^{15}\ \mathrm{min^{-1}}$, $\beta = 1$°C $\mathrm{min^{-1}}$. *n*th order analyses: $n = 0.669$, $E_n = 220.2$ kJ $\mathrm{mol^{-1}}$, $A_n = 3.87 \times 10^{15}\ \mathrm{min^{-1}}$.

Curves K and F were generated using the Kissinger and Friedman parameters given in Table 3. The uncorrected iso-conversional pre-exponential factors were used in generating curve F. These factors do not correlate with the constant activation energy values. On the other hand, the model-corrected pre-exponential factors exhibit a compensation relationship with the iso-conversional activation energies, E_F, as shown in Table 3. The crosses on the actual model $1-\alpha$ versus T curves indicate the T_α values computed using the model-corrected pre-exponential factors. The effect of the correction is dramatic, particularly in the case of the A2 and D4 models. In the case of model R3, the actual and the K and F curves are so close as to be well-nigh indistinguishable. Analogous calcula-

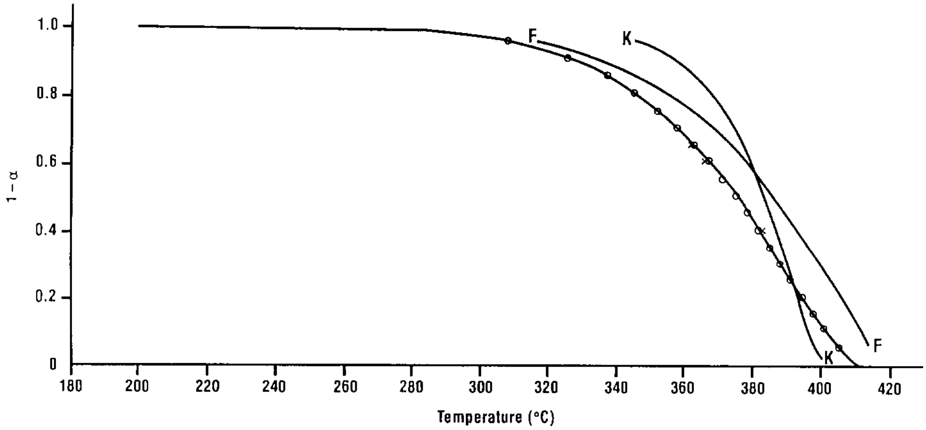

Fig. 3. Model D4: $E = 220$ kJ $\mathrm{mol^{-1}}$, $A = 1.25 \times 10^{15}\ \mathrm{min^{-1}}$, $\beta = 1$°C $\mathrm{min^{-1}}$. *n*th order analyses: $n = 0.436$, $E_n = 105.5$ kJ $\mathrm{mol^{-1}}$, $A_n = 5.99 \times 10^{6}\ \mathrm{min^{-1}}$.

Table 3

Kissinger and Friedman reaction *n*th order kinetics parameters

Model [2]	E_K/(kJ mol^{-1})	A_K/min^{-1}	$\bar{E}_F$/(kJ mol^{-1})	$\ln A_F{}^a = k_1 \cdot E_F + k_2$		
				k_1	k_2	r^2
A2	219.94	1.189×10^{15}	219.71 ± 0.54	0.1604	−0.4968	0.9956
R3	220.05	3.781×10^{15}	219.87 ± 0.63	0.1664	−1.8165	0.9986
D4	220.39	12.622×10^{15}	220.24 ± 1.21	0.1721	−3.071	0.9952

[a] Model-corrected pre-exponential factors.

tions on the remaining single solid state reaction systems listed in Table 1 have yielded agreements similar to those described above.

3. Conclusions

Despite the large disparities in the magnitude of the actual solid state model kinetics parameters compared with the *n*th order equivalent values, extents of reaction as a function of temperature data at any heating rate, computed using the *n*th order Arrhenius analysis parameters, are identical with those calculated using iso-conversionally determined kinetics parameters, with the appropriately model-corrected pre-exponential factors. Since the iso-conversionally determined parameter values are the correct ones, *n*th order Arrhenius analysis of single heating rate data should be sufficient to postulate the correct mechanism and determine, using the "ratio calculation" procedure [1], the energetic and entropic system parameters, i.e. solve the inverse kinetics problem [9]. Superficially, one can conclude that multiple heating rate, non-isothermal experiments are unnecessary. For single reaction system model studies, this is true. However, in the case of real systems, one must clearly establish that a single reaction is occurring. As has been shown for a number of multiple mutually independent model systems [6], when treated empirically as *n*th order processes, the order is a logarithmic function of the heating rate. Furthermore, it has been clearly demonstrated that the iso-conversional activation energies for such systems vary considerably with extent of reaction. The character of the variation is highly dependent upon the number of single members of the multiple set, and the magnitudes of their individual kinetics parameters. In order to ratify the singularity of a real system undergoing any form of thermochemical reaction, it is absolutely necessary that multiple heating rate thermoanalytical experiments be carried out.

As a case in point, the thermal degradation of calcium oxalate monohydrate was recently examined at various heating rates [1]. *n*th order Arrhenius analyses at each heating rate together with peak analysis of the entire data set strongly indicated the D4, R3 and D4 models for the three stages, dehydration and sequential loss of carbon monoxide and carbon dioxide. Despite the constant value of n over a 100-fold change in heating rate for each of these steps, indicating an apparent single reaction, iso-conversional analysis has shown that the activation energy is not constant but in the range $0.15 \leq \alpha \leq 0.95$ E_F varies linearly with extent of reaction. In the case of the second stage, postulated as conforming to the contracting volume mechanism, some success was achieved. Over the range $0.15 \leq \alpha \leq 0.95$, the Friedman iso-conversional activation energy follows the relationship: E_F (kJ mol^{-1}) $= 260.2 + 10.5\alpha$ ($r^2 = 0.928$). This slight increase with extent of the thermal degradation of the anhydrous calcium oxalate may be due to the fact that, in reality, the particles will not be truly spherical, as demanded by theory, and are of unknown size distribution. However, the constancy of the order of reaction [1], i.e. 0.66 ± 0.01, together with the fact that the Friedman parameters follow the compensation relationship $\ln(A_F) = 0.186E_F - 8.114$ ($r^2 = 0.999$) strengthens the postulation of essentially a singular R3 reaction. In the case of the first, dehydration stage, the Friedman activation energy decreases sharply in the early stages of the reaction but then decreases more slowly during the remainder of the dehydration. Qualitatively, the $E_F - \alpha$ variation is analogous to that described by Masuda et al. [10]. Although a compensation $\ln A_F - E_F$ is obtained, indicative of a single reaction, the order of reaction does increase slightly with heating rate [1]. In the final stage, the degradation of calcium carbonate, the iso-conversional activation energy exhibits analogous behavior with increasing extent of reaction as the dehydration. Again, a compensation $\ln A_F - E_F$ relationship is observed, and the order of the reaction remains constant at 0.42 [1]. For both the first and third stages, when the model D4-corrected nth order iso-conversional data are used to calculate T_α as a function of the extent of reaction, according to Eq. (5), there are significant deviations from the original experimental data. Calculations have shown that the monitored $E_F - \alpha$ variations do not conform to a multiple model set of mutually independent reactions. It is considered that a more probable explanation lies in a competition between two mechanisms, the contributions of both to the overall reaction varying with the extent of the reaction, as originally proposed by Masuda et al. [10] for the first dehydration stage. Model calculations, aimed at investigating changing mechanisms with reaction extent, are in progress.

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