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THE GENERAL APPLICABILITY OF THE KISSINGER EQUATION IN THERMAL ANALYSIS*

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Computer modelling calculations will be presented which verify the fact that, if a single reaction follows either Arrhenius or transition state kinetic theory over its entire extent, then the maximum rate of reaction data obeys the modified Kissinger equation, irrespective of the applicable kinetic model. The magnitude of the Kissinger parameter correction term is dependent on the model, ranging from about 0.4% for nth order and random nucleation, Avrami–Erofeev models to 17% for three dimensional diffusion controlled reactions. The consequences of selecting the incorrent kinetic model in interpreting experimental thermoanalytical data will be examined, thereby giving a rational explanation for the wide range of published kinetic parameters for a number of solid state decompositions.

Amongst the several thermoanalytical techniques available, thermogravimetry, in particular, provides an excellent means for studying the kinetics of single reactions and multiple processes. Although the isothermal technique is favored, non-isothermal thermogravimetry offers several advantages. This is very much the case when the complex multiple degradative reactions involved in fossil fuel pyrolysis are investigated [1, 2]. In such situations, one cannot utilize the isothermal technique with any confidence, since nothing can be said regarding the reactions occurring prior to the system attaining the isothermally set temperature.

Over the last three decades, a number of kinetic analysis schemes, based upon relationships between the temperature at which the reaction rate attains a maximum value and the heating rate have been proposed. Perhaps the most well-known relationships are identified with the names of Kissinger [3] and Ozawa [4]. In recent years the use of the Ozawa equation has gained popularity. The Kissinger equation has been criticized, since as originally postulated, it is applicable only to the most simple processes, namely single first order reactions.

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Recently, the author has proposed a generalized form of the Kissinger equation [5], and has used it successfully in studying multiple reaction schemes [6]. It is the purpose of this paper to extend the treatment of this aspect of non-isothermal kinetic analysis, and show the wide applicability of the generalized Kissinger equation.

Summary of theoretical aspects

If the rate of a thermally-induced reaction follows the general relationship

$$\mathrm{d}\alpha/\mathrm{d}t = A \cdot T^m \cdot e^{-E/RT} \cdot f(\alpha) \tag{1}$$

where α is the dimensionless degree of reaction and $f(\alpha)$ is the kinetic model α dependency with T, R, A, and E having their usual significance*, then as shown [5] it also obeys the generalized Kissinger equation.

$$\ln\left(\beta/T_{max}^{m+2}\right) = \ln(AR/E) + \ln \Phi_m(\alpha_{max}) - E/RT_{max} \tag{2}$$

where

$$\Phi_m(\alpha_{max}) = \frac{-f'(\alpha_{max})}{(1 + mRT_{max}/E)} \tag{3}$$

If one makes the Arrhenius assumption, the temperature exponent, $m = 0$. However, transition state theory predicts $m = 1$. The integral form of the rate equation, from which Ozawa's equation is derived at $\alpha = \alpha_{max}$, is given by the general relationship [5], equation (4), with the exponential integral p-function given by equation (5).

$$F(\alpha) = A/(\beta \cdot (m+1)) \cdot (E/R)^{m+1} \cdot p_m(E/RT) \tag{4}$$

$$p_m(E/RT) = \exp(-E/RT) \cdot (RT/E)^{m+2} \cdot \gamma_m(E/RT) \tag{5}$$

In deriving his equation for the case $m = 0$, Ozawa [4] made two assumptions to express the p-function. Initially, only the first term (unity) of the polynomial, $\gamma_0(E/RT)$, was used, which means that for nth order reactions, $F(\alpha_{max}) = 1$. However, he then used Doyle's linear approximation to express the p-function [7]. The development of this equation was based upon the use of the three-term Schlömilch expansion for the polynomial $\gamma_0(E/RT)$ (see Blazejowski [8] for details). One cannot use both approximations in such a derivation.

The function $-f'(\alpha_{max})$ has been given [5] for a number of solid state kinetic model functions, tabulated, for example, by Brown, Dollimore and Galwey [9]. In

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* See glossary of symbols, p. 668.

what follows, the various models will be designated by their commonly used symbols [10]. In order to develop degree and rate of reaction data for these models, a FORTRAN program, written originally to generate such data for single and multiple first order reactions [6], has been generalized. During the preparation of the more extensive and complex program, two errors in the integral and differential forms of the $f(\alpha)$ function for three dimensional diffusion controlled processes [5] were discovered and corrected, as shown in the appendix.

Application to various kinetic models

A hypothetical reaction, with an activation energy, E, of 220 kJ · mol^{-1}, and a pre-exponential factor, A, of 10^{15} min^{-1}, is considered. Figures 1 and 2 show the complement of the extent of reaction $(1-\alpha)$ and the rate of reaction $(d\alpha/dt)$, respectively, at a heating rate of 10 deg min^{-1} for nine different models. The numerals 1 and 2 indicate first and second order reactions (F, 1; F, 2). 3 and 4

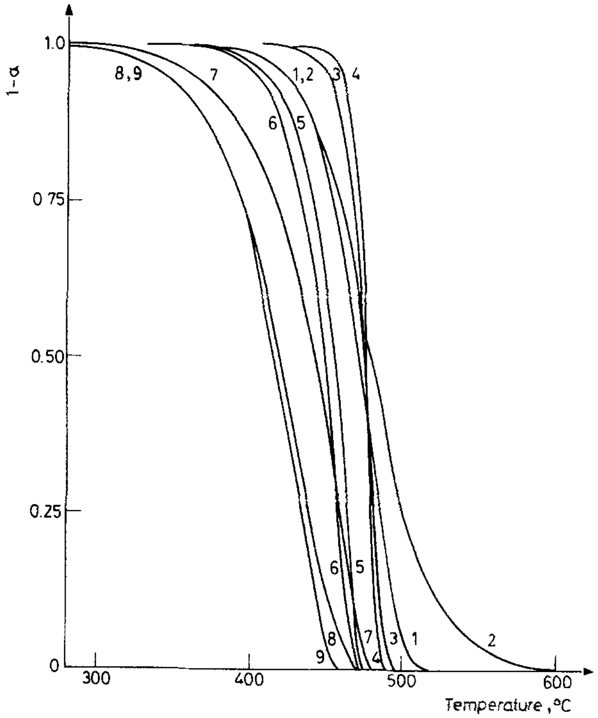

Fig. 1 Complementary extent of reaction $(1-\alpha)$ as a function of temperature at $\beta = 10°\mathrm{C \cdot min^{-1}}$ calculated for $E = 220$ kJ · mol^{-1}, $A = 10^{15}$ min^{-1} $(m=0)$. 1–9, models F1, F2, A2, A3, R2, R3, D2, D3, and D4

indicate the Avrami–Erofeev two and three dimensional bulk growth of nuclei models (A2; A3). 5 and 6 refer to two and three dimensional phase boundary movement models (R2; R3). 7 indicates the two dimensional diffusion control model (D2). Three dimensional diffusion control has been described by the Jander and Ginstling–Brounshtein equations. 8 and 9 refer to these two models, D3 and D4, respectively.

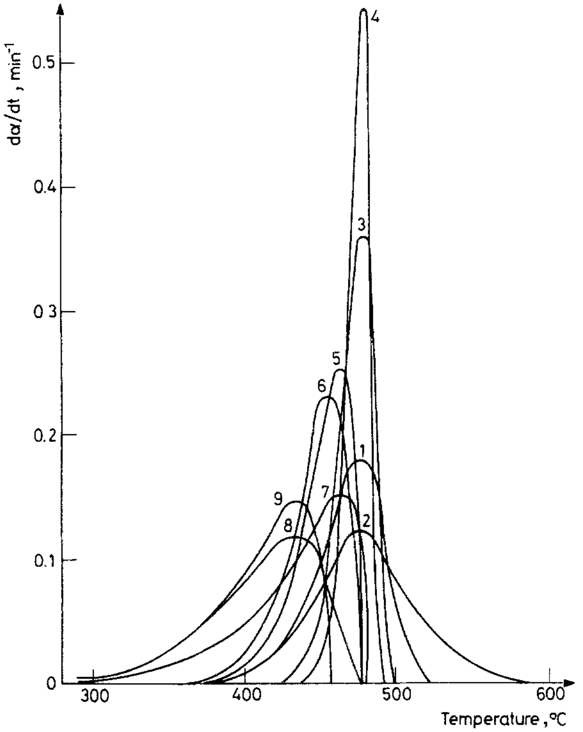

Fig. 2 Rate of reaction (dα/dt) as a function of temperature at $\beta = 10°C \cdot min^{-1}$ calculated for $E = 220$ kJ·mol^{-1}, $A = 10^{15}$ min^{-1} ($m = 0$). 1–9, models F1, A2, A3, R2, R3, D2, D3, and D4

As can be seen, there are significant differences in both the positions relative to temperature and the characteristic contours of the several curves. Thus, for example, reactions under three dimensional diffusion control [8, 9] are 90–95% completed prior to the onset of n^{th} order or Avrami–Erofeev reactions [1–4] with identical energetic parameters. The latter type reactions are particularly characterized by very narrow temperature boundaries between onset and completion, whereas n^{th} order reactions are typified by broader rate of reaction curves. As n increases, so the tailing edge of the curves becomes more extended. Contrary to this, diffusion controlled reactions [7–9], particularly three dimensional, exhibit a broad leading edge and a sharp tailing region. The phase boundary movement models [5, 6] exhibit behaviour somewhere between these two extremes, but like the diffusion-controlled models, the leading edge is relatively broader than the tailing region.

From similar data to that shown in figures 1 and 2, generated for heating rates from 1 deg min^{-1} to 100 deg min^{-1}, α_{max} and T_{max} values were calculated, and Kissinger analyses, with and without the logarithmic correction term in equation (2), were performed. Typical uncorrected (U) and corrected (C) Kissinger plots for case $m=0$ are shown in Figure 3 for two models, a second order reaction (F, 2 $-2U/C$) and a three dimensional diffusion-controlled model ($9U$ and $9C$), described by the Ginstling–Brounshtein equation [5] (D4). For comparison, similar plots for the case $m=1$ are shown. In this case, the Arrhenius pre-exponential factor, A, was changed to 10^{12} K^{-1} min^{-1}. As can be seen, both the uncorrected and corrected Kissinger plots are linear and essentially parallel. For the second order model, the plots are essentially indistinguishable. However, for the D4 model, there is a significant change in the intercept.

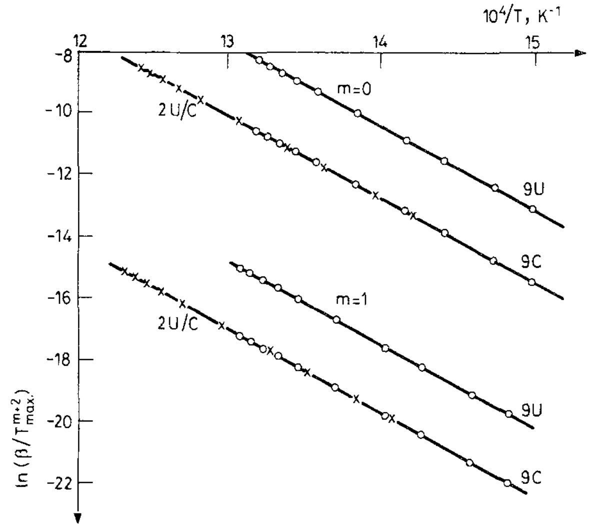

Fig. 3 Typical Kissinger plots, uncorrected (U) and corrected (C) for models F2 (2), legend X and D4 (9), legend 0, calculated for $E = 220$ kJ·mol^{-1}, and $A = 10^{15}$ min^{-1} ($m=0$) and $A = 10^{12}$K^{-1}·min^{-1} ($m=1$)

The correction terms for each of the several models considered are listed for both cases $m=0$ and $m=1$ at the two extreme heating rates in tables 1a and 1b, respectively. The change in α_{max} with heating rate is minimal, namely $<0.6\%$ sK^{-1}, for all kinetic models. The logarithmic correction terms in the modified Kissinger equation are, with the exception of the three-dimensional diffusion-controlled

Table 1a Modified Kissinger Equation Correction Terms for Various Models
Arrhenius Parameters: $E = 220\ \mathrm{kJ \cdot mol^{-1}}$ $A = 10^{15}\ \mathrm{min^{-1}}$

	$\beta = 1\ ^\circ\mathrm{C \cdot min^{-1}}$			$\beta = 100\ ^\circ\mathrm{C \cdot min^{-1}}$		
Model	$\alpha_{\max}$	$\ln \Phi_0(\alpha_{\max})$	$\frac{\ln \Phi_0(\alpha_{\max})}{\ln(\beta/T^2_{\max})}$ (%)	$\alpha_{\max}$	$\ln \Phi_0(\alpha_{\max})$	$\frac{\ln \Phi_0(\alpha_{\max})}{\ln(\beta/T^2_{\max})}$ (%)
F, 1	0.6145	0	0	0.6103	0	0
F, 2	0.4741	0.049	−0.37	0.4720	0.054	−0.62
A2	0.6216	−0.039	0.30	0.6207	−0.043	0.49
A3	0.6286	−0.046	0.35	0.6247	−0.051	0.58
R2	0.7379	0.668	−5.1	0.7361	0.665	−7.6
R3	0.6866	1.082	−8.3	0.6874	1.080	−12.4
D2	0.8130	0.643	−4.9	0.8105	0.646	−7.4
D3	0.6728	2.284	−17.6	0.6705	2.295	−26.6
D4	0.7526	2.215	−17.0	0.7484	2.222	−25.7
B1*	0.8174	−0.455	3.5	0.8164	−0.458	5.2

*Model valid only for $\alpha \geqslant 0.5$

Table 1b Modified Kissinger Equation Correction Terms for Various Models
Transition State Parameters: $E = 220\ \mathrm{kJ \cdot mol^{-1}}$ $A = 10^{12}\ \mathrm{K^{-1} \cdot min^{-1}}$

	$\beta = 1\ ^\circ\mathrm{C \cdot min^{-1}}$			$\beta = 100\ ^\circ\mathrm{C \cdot min^{-1}}$		
Model	$\alpha_{\max}$	$\ln \Phi_1(\alpha_{\max})$	$\frac{\ln \Phi_1(\alpha_{\max})}{\ln(\beta/T^3_{\max})}$ (%)	$\alpha_{\max}$	$\ln \Phi_1(\alpha_{\max})$	$\frac{\ln \Phi_1(\alpha_{\max})}{\ln(\beta/T^3_{\max})}$ (%)
F, 1	0.6151	−0.027	0.13	0.6100	−0.030	0.19
F, 2	0.4772	0.022	−0.11	0.4738	0.022	−0.15
A2	0.6228	−0.065	0.33	0.6205	−0.072	0.46
A3	0.6305	−0.072	0.36	0.6245	−0.079	0.51
R2	0.7365	0.642	−3.3	0.7356	0.637	−4.1
R3	0.6896	1.056	−5.4	0.6888	1.052	−6.8
D2	0.8156	0.614	−3.1	0.8103	0.616	−4.0
D3	0.6759	2.257	−11.6	0.6704	2.264	−14.8
D4	0.7531	2.188	−11.2	0.7511	2.189	−14.3
B1*	0.8184	−0.481	2.4	0.8157	−0.487	3.1

*Model valid only for $\alpha \geqslant 0.5$

models, relatively small. Irrespective of their magnitude, the application of the modified Kissinger equation yields correct kinetic parameter values in all cases, as shown in tables 2a and 2b. If there is doubt as to the correct kinetic model to be used in calculating the correction term, little is lost. Kissinger analyses were performed on the data, assuming in all cases a $(1-\alpha)^n$ model. The results are shown in the sixth and seventh columns of tables 2a and 2b. Again, one finds that the E values are insensible

Table 2a Modified Kissinger Equation Kinetic Parameters
Arrhenius Parameters: $E = 220\ \mathrm{kJ \cdot mol^{-1}}$ $A = 10^{15}\ \mathrm{min^{-1}}$

	Uncorrected		Corrected actual model		Corrected $(1-\alpha)^n$ model	
Model	E, kJ · mol^{-1}	$A \cdot 10^{-15}$ min^{-1}	E, kJ · mol^{-1}	$A \cdot 10^{-15}$ min^{-1}	E, kJ · mol^{-1}	$A \cdot 10^{-15}$ min^{-1}
F, 1	220.2	1.024	220.2	1.024	220.2	1.024
F, 2	220.2	1.090	220.0	0.992	220.0	0.992
A2	219.5	0.887	219.7	0.959	219.6	0.892
A3	219.8	0.922	220.0	1.011	219.8	0.920
R2	219.8	1.890	220.0	0.993	220.0	1.987
R3	219.8	2.838	219.9	0.977	219.9	2.936
D2	220.0	1.914	219.9	0.988	220.3	2.065
D3	220.5	10.770	220.0	0.990	220.6	11.210
D4	220.0	9.280	219.9	0.979	220.3	9.895
B1*	219.7	0.608	219.9	0.978	220.0	0.654

*Model valid only for $\alpha \geqslant 0.5$

Table 2b Modified Kissinger Equation Kinetic Parameters
Transition State Parameters: $E = 220\ \mathrm{kJ \cdot mol^{-1}}$ $A = 10^{12}, \mathrm{K^{-1} \cdot min^{-1}}$

	Uncorrected		Corrected actual model		Corrected $(1-\alpha)^n$ Model	
Model	E, kJ · mol^{-1}	$A \cdot 10^{12}$, K^{-1} · min^{-1}	E, kJ · mol^{-1}	$A \cdot 10^{12}$, K^{-1} · min^{-1}	E, kJ · mol^{-1}	$A \cdot 10^{12}$, K^{-1} · min^{-1}
F, 1	220.0	0.971	220.2	1.029	220.2	1.029
F, 2	220.3	1.066	220.2	1.037	220.2	1.037
A2	219.8	0.899	220.1	1.021	219.9	0.949
A3	219.8	0.891	220.1	1.023	219.9	0.940
R2	219.7	1.810	220.0	1.000	220.0	2.000
R3	219.6	2.669	219.8	0.970	219.8	2.915
D2	220.1	1.869	220.1	1.015	220.5	2.123
D3	220.6	10.660	220.3	1.046	220.9	11.710
D4	220.1	9.060	220.0	0.998	220.4	10.170
B1*	220.0	0.615	220.3	1.046	220.3	0.694

*Model valid only for $\alpha \geqslant 0.5$

to the model selected, and the A values are similar in magnitude to those obtained by analyzing without correction, as shown in the second and third columns of these tables. The n values are of the order shown in tables 3 and 4. In certain cases, one obtains exactly what is expected. Thus, for the two and three-dimensional phase boundary movement models, R2 and R3, one has $f(\alpha) = 2\cdot(1-\alpha)^{1/2}$, and $3\cdot(1-\alpha)^{2/3}$, respectively. This analysis confirms one obvious difficulty, namely the distinguishing of Avrami–Erofeev reactions, A2 and A3, from simple first order reactions, F1.

Table 3a Arrhenius analysis kinetic parameters,
$f(\alpha) = (1-\alpha)^n$ assumption
Model kinetic parameters: $E = 220\ \mathrm{kJ\cdot mol^{-1}}$ $A = 10^{15}$, $\mathrm{min^{-1}}$
$\beta = 1 - 150\ ^\circ\mathrm{C\cdot min^{-1}}$

Model	E, $\mathrm{kJ\cdot mol^{-1}}$	A, $\mathrm{min^{-1}}$	n
A2	451 – 452	$230 - 2\cdot 10^{30}$	1.0
A3	683 – 685	$4700 - 3\cdot 10^{45}$	1.0
R2	220 ± 0.1	$1.99 \pm 0.04\cdot 10^{15}$	0.50
R3	220 ± 0.2	$3.02 \pm 0.09\cdot 10^{15}$	0.67
D2	104.3 ± 0.14	$1.9 - 25.1\cdot 10^{6}$	0.27
D3	106 – 105	$5.54 - 61.8\cdot 10^{6}$	0.67
D4	105 – 104	$4.88 - 55.9\cdot 10^{6}$	0.43
B1	220.8 ± 0.1	$3.5 \pm 0.05\cdot 10^{14}$	0.29

Table 3b Arrhenius analysis kinetic parameters,
$f(\alpha) = (1-\alpha)^n$ assumption
Model kinetic parameters: $E = 220\ \mathrm{kJ\cdot mol^{-1}}$ $A = 10^{12}$, $\mathrm{K\cdot min^{-1}}$
$\beta = 1 - 150\ ^\circ\mathrm{C\cdot min^{-1}}$

Model	E, $\mathrm{kJ\cdot mol^{-1}}$	A, $\mathrm{K^{-1}\cdot min^{-1}}$	n
A2	457 – 459	$426 - 4\cdot 10^{27}$	1.0
A3	694 – 698	$1473 - 0.1\cdot 10^{44}$	1.0
R2	220.1 ± 0.2	$2.04 \pm 0.07\cdot 10^{12}$	0.50
R3	220.1 ± 0.3	$3.04 \pm 0.17\cdot 10^{12}$	0.67
D2	100.7 ± 0.47	$1.44 - 14.4\cdot 10^{3}$	0.27
D3	103 – 102	$4.30 - 42.0\cdot 10^{3}$	0.67
D4	103 – 101	$4.00 - 37.4\cdot 10^{3}$	0.43
B1	220.3 ± 0.2	$3.24 \pm 0.09\cdot 10^{11}$	0.29

It is pertinent at this point to consider what happens if an Arrhenius analysis is performed on extent and rate of reaction data, generated for the several different kinetic models, assuming the data conforms to an n'th order model. Such a set of analyses have been carried out for each model at each heating rate used in the

Table 4a Friedman analysis kinetic parameters
Model parameters: $E = 220$ kJ · mol^{-1} $A = 10^{15}$ min^{-1} $\beta = 1 - 150$ °C · min^{-1}

	Actual model		$(1-\alpha)^n$ model		
Model	E, kJ · mol^{-1}	$A \cdot 10^{-15}$, min^{-1}	E, kJ · mol^{-1}	$A \cdot 10^{-15}$, min^{-1}	n
F1	220.02 ± 0.03	1.003 ± 0.004	220.02 ± 0.03	1.003 ± 0.004	1.0
F2	220.00 ± 0.02	1.000 ± 0.003	220.02 ± 0.02	1.000 ± 0.003	2.0
A2	220.14 ± 0.27	1.012 ± 0.023	220 – 225.2	0.45 – 7.33	1.0
A3	219.4 ± 1.86	0.943 ± 0.277	219.9 ± 0.485	0.41 – 4.73	1.0
R2	220.00 ± 0.043	1.000 ± 0.006	220.0 ± 0.024	1.99 ± 0.007	0.5
R3	220.03 ± 0.079	1.005 ± 0.011	220 – 214	2.99 – 1.10	0.67
D2	220.02 ± 0.064	1.003 ± 0.009	220 – 219.6	19.71 – 1.09	0.27
D3	220.01 ± 0.030	1.002 ± 0.004	220 – 217.8	87.96 – 1.66	0.67
D4	220.00 ± 0.033	1.000 ± 0.005	220 – 219	87.82 – 2.92	0.43
B1*	220.00 ± 0.008	1.000 ± 0.001	220 – 221	0.31 – 0.13	0.29

$^*0.50 < \alpha < 0.95$

Table 4b Friedman analysis kinetic parameters
Model parameters: $E = 220$ kJ · mol^{-1} $A = 10^{12}$ K · min^{-1} $\beta = 1 - 150$ °C · min^{-1}

	Actual model		$(1-\alpha)^n$ model		
Model	E, kJ · mol^{-1}	$A \cdot 10^{-12}$, min^{-1}	E, kJ · mol^{-1}	$A \cdot 10^{-12}$, min^{-1}	n
F1	220.02 ± 0.05	1.003 ± 0.006	220.02 ± 0.05	1.003 ± 0.006	1.0
F2	220.01 ± 0.02	1.001 ± 0.003	220.01 ± 0.02	1.001 ± 0.003	2.0
A2	220.05 ± 0.13	1.005 ± 0.019	220 – 221.3	0.45 – 3.71	1.0
A3	219.6 ± 0.82	0.945 ± 0.110	220.0 ± 0.60	0.42 – 3.21	1.0
R2	220.05 ± 0.21	1.007 ± 0.003	220.06 ± 0.22	2.022 ± 0.07	0.5
R3	220.02 ± 0.08	1.002 ± 0.010	220 – 219.5	2.99 – 2.77	0.67
D2	220.0 ± 0.03	1.000 ± 0.003	220 – 219	19.62 – 0.65	0.27
D3	220.00 ± 0.04	1.001 ± 0.005	220 – 217.5	87.26 – 1.56	0.67
D4	220.0 ± 0.02	1.000 ± 0.003	220 – 217.9	87.44 – 2.20	0.43
B1*	220.0 ± 0.01	1.000 ± 0.002	220 – 220.4	0.32 – 0.12	0.29

$^*0.50 < \alpha < 0.95$

preceding Kissinger analysis. The results are summarized in tables 3a and 3b, and are quite startling. One obtains kinetic parameters extending over an extremely wide range of values, very large for the Avrami–Erofeev (A2, A3) model input data, very small for the diffusion-controlled (D2, D3, D4) model input data. One questions the utility of performing an Arrhenius analysis on one set of data.

To clarify the situation, Arrhenius analyses at fixed extents of reaction (α = 0.05–0.95), namely Friedman [11] analyses, were carried out on the same input data obtained at the several heating rates used for the Kissinger analyses, assuming both the correct and an n^{th} order reaction model. The results are summarized in tables 4a and 4b. The distortions in the Arrhenius analysis kinetic parameters, resulting from the incorrect choice of kinetic model, essentially disappear since one utilizes data at the same $f(\alpha)$ values in the Friedman analysis, emphasizing the utility of this procedure in analyzing thermal data. One obtains essentially the correct E values with mildly incorrect A values, which change slightly with extent of reaction. A comparison of the results of tables 2 and 4 shows that the modified Kissinger and Friedman analysis derived kinetic parameters are in very good agreement.

Conclusions

The modified Kissinger equation is generally applicable in analyzing thermally induced extent and rate of reaction data, yielding correct values for the kinetic parameters, the energy of activation, E, and the pre-exponential factor, A. One should proceed with caution in assessing the results of Arrhenius analyses of non-isothermal reaction rate data. Injudicious choice of reaction model can result, in certain cases, in incorrect values of kinetic parameters of widely varying magnitude, as emphasized in tables 3a and 3b. Thus, Zsakó and Arz [12] quote an extremely wide range of kinetic parameters reported for the calcination of calcium carbonate, a number of which are unbelievable. Since one can only be certain of obtaining correct values by following the Friedman procedure, which necessitates acquiring data at several heating rates, one can easily perform the Kissinger analysis. Even if the simple form of equation (2), without the logarithmic correction term, is used, the resulting E values are correct. In utilizing the correct form of the equation, even if the reaction model selected is incorrect, the resulting A values are of the correct order of magnitude.

A number of factors may be used to assist one choose the correct kinetic model. The value of α_{max} at $(d\alpha/dt)_{max}$ is specific for a model. Since the values do vary slightly with heating rate and for a number of models are close, one should consider also the character of the extent and rate of reaction curves in making the decision. If one assumes an n^{th} order reaction, n may be easily calculated from a knowledge of α_{max}, as previously indicated [5]. The resulting value also assists the decision. Finally, from a Friedman analysis, the direction and order of magnitude of the change in A with α is also helpful in the final analysis.

Several of the algorithms and procedures developed for this generalized model calculation program have been incorporated into a thermogravimetric data analysis program which the author is currently using to interpret data for several interesting solid state reactions in the mineral and fossil fuel field, to be reported in the near future.

Appendix

The kinetic model parameters used in calculating the correction term in the modified Kissinger equation (2) have been given previously [5]. For the Jander model for three dimensional diffusion control, D3, the $f(\alpha)$ function quoted by Blazejowski et al. [13], which contains a typographical error, was used without checking, resulting in incorrect equations for α_{max}, $F(\alpha_{max})$ and $-f'(\alpha_{max})$. The correct forms are given by Sestak and Berggren [14]. In the case of the Ginstling–Brounshtein model, D4, a typographical error has been noted in the equations previously given [5]. The author apologizes for these mistakes, which are rectified, as shown below. The reader is referred to the original paper [5] for the definition of the η function. The equation numbers are as previously given [5].

Jander model (D3

$$f(\alpha) = \frac{3\cdot(1-\alpha)^{1/3}}{2\cdot[(1-\alpha)^{-1/3}-1]} \tag{17}$$

$$\alpha_{max} = 1-(\eta+1/2)^{-3} \tag{17a}$$

$$F(\alpha_{max}) = [(\eta-1/2)/(\eta+1/2)]^2 \tag{17b}$$

$$-f'(\alpha_{max}) = \eta\cdot[(\eta+1/2)/(\eta-1/2)]^2 \tag{17c}$$

Ginstling–Brounshtein Model (D4)

$$f(\alpha) = \frac{3}{2\cdot[(1-\alpha)^{-1/3}-1]} \tag{18}$$

$$\alpha_{max} = 1-[1/6\eta+(1/36\eta^2+1/6\eta)^{1/2}]^3 \tag{18a}$$

$$F(\alpha_{max}) = 1-\frac{2\cdot\alpha_{max}}{3}-(1-\alpha_{max})^{2/3} \tag{18b}$$

$$-f'(\alpha_{max}) = \frac{1}{2\cdot(1-\alpha_{max})^{2/3}\cdot[(1-\alpha_{max})^{1/3}-1]^2} \tag{18c}$$

Glossary of symbols

α	extent of reaction (dimensionless)
$d\alpha/dt$	rate of reaction (min^{-1})
$f(\alpha)$	general expression for kinetic model
$F(\alpha)$	general expression for the integral of the inverse $f(\alpha)$ function
T	absolute temperature (K)
E	energy of activation (kJ $\cdot$ mol^{-1})
A	pre-exponential factor (K$^{-m}\cdot$ min^{-1})
m	exponent of weak temperature term in rate equation (1)
R	universal gas constant (8.31434 kJ $\cdot$ mol^{-1} K^{-1})
β	heating rate (deg. min^{-1} or K $\cdot$ min^{-1})
$p_m(E/RT)$	general function including the exponential temperature integral

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Zusammenfassung — Computer-Modellberechnungen werden dargelegt, die die Tatsache bestätigen, daß die maximale Reaktionsgeschwindigkeit unabhängig vom angewandten Modell von der modifizierten Kissinger-Gleichung beschrieben wird, wenn eine einzelne Reaktion über den gesamten Verlauf hinweg entweder der kinetischen Arrhenius- oder der Übergangszustands-Theorie folgt. Die Größe der Kissinger-Parameter hängt vom Modell ab und liegt zwischen 0,4% für Avrami–Erofeev-Modelle mit n-ter Ordnung und ungeordneter Kristallkeimbildung und 17% für dreidimensionale diffusionskontrollierte Reaktionen. Die bei Wahl eines falschen kinetische Modells für die Interpretierung thermoanalytischer Daten eintretenden Folgen werden untersucht, wobei eine vernünftige Erklärung für die große Streuung von publizierten kinetischen Parametern einer Anzahl von Festkörperzersetzungsreaktionen gegeben wird.

Резюме — Представлены компьютерные модельные расчеты, подтверждающие, что если единственная реакция полностью подчинается уравнению Аррениуса или теории переходного кинетического состояния, тогда максимальная скорость реакции подчиняется видоизмененному уравнению Киссинджера, независимо от применяемой кинетической модели. Значение параметра Киссинджера коррекционного множителя зависит от взятой модели и изменяется от 0,4% дла *n*-порядка реакции и модели произвольного образования центров кристаллизации модели Аврами-Ерофеева до 17% — для модели трехразмерных диффузионно-контролируемых реакций. Исследованы последствия выбора неправильной кинетической модели при интерпретации экспериментальных термоаналитических данных, давая к этому рациональное объяснение широкому интервалу публикуемых кинетических параметров ряда твердотельных реакций разложения.