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KNIS—a computer program for the systematic kinetic analysis of non-isothermal thermogravimetric data

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Abstract

A computer program for the derivation of kinetic parameters from non-isothermal thermogravimetric data is presented. The system enables an automatic regional kinetic analysis of the overall derived data. The program includes 12 solid state decomposition mechanism models. The software is designed to be flexible and user friendly.

INTRODUCTION

A knowledge of the relevant kinetic behaviour is important for the comprehensive evaluation of solid state reaction processes. The kinetic parameters of a decomposition process can be calculated from the relevant non-isothermal thermogravimetric data, and many kinetic analysis programs are available. Zsako and Zsako [1] have described a computer program to calculate the kinetic parameters from non-isothermal thermogravimetric data for solid state degradative reactions. However, this program is limited to *n*th order reactions. Reich and Stivala [2] have described a BASIC program which incorporates ten theoretically possible solid state decomposition mechanisms. A FORTRAN program for the kinetic analysis of transposed non-isothermal TG data has been developed by Elder [3] which is based upon the Arrhenius, Friedman and Kissinger analysis procedures and includes a maximum of nine different solid state rate-controlling reactions. Eftimie and Segal [4] have reported a BASIC program to obtain non-isothermal kinetic parameters based upon the Coats–Redfern method; a later FORTRAN-77 version has been developed [5]. Taylor and Khanna [6] have described a program for the kinetic evaluation of TG data from a single non-isothermal experiment using the computerized method of Skvara and Sestak [7]. Recently Malek [8] has reported kinetic analysis software for experimental DSC data.

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It is often desirable to perform a regional kinetic analysis of the entire derived data, especially for multistep mechanism processes such as coal pyrolysis, which generally occurs in two stages. Most of the programs presently available are not adaptable to such an analysis. In the Skvara and Sestak method [7], three α–T regions are considered: the initial ($\alpha = 0.03$–0.35), the intermediate ($\alpha = 0.3$–0.8) and the final ($\alpha = 0.7$–0.97). However, this procedure cannot ensure a "best" fit across the entire experimental range.

The aim of this paper is to describe a new computer program, KNIS, for the kinetic analysis of non-isothermal thermogravimetric data, which enables an automatic regional kinetic analysis of the entire TG data obtained. The program includes 12 theoretically possible solid state decomposition mechanism models. It is flexible and user friendly.

KINETIC EQUATIONS

The rate expression for a non-isothermal reaction is assumed as

$$\frac{d\alpha}{dt} = A\,e^{-E/RT} f(\alpha) \tag{1}$$

where α is the degree of conversion and $f(\alpha)$ depends on the mechanism of the process. With a constant heating rate, $\beta = dT/dt$, integration of eqn. (1) leads to

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = F(\alpha) = \frac{EA}{R\beta} p(x) \tag{2}$$

the logarithmic form of which is

$$\log F(\alpha) = \log\left(\frac{AE}{\beta R}\right) + \log p(x) \tag{3}$$

A truncated Schlomilch expansion [9] is used:

$$p(x) = \exp(-x)(1/x)[1/(x+2)] \tag{4}$$

where $x = E/RT$.

Several kinetic models have been proposed, as listed in Table 1 together with the form of $f(\alpha)$ and $F(\alpha)$ used.

DESCRIPTION OF THE PROGRAM

The KNIS program is shown schematically in Fig. 1, and is written in FORTRAN-77. There are two data input forms: interactive and file. In the latter case, the experimental data file is created by a DATA-INPUT subroutine. The kinetic models incorporated in the system include those shown

TABLE 1

Kinetic models incorporated into the KNIS program

Model	Symbol	$f(\alpha)$	$F(\alpha)$
Coats–Redfern[a]	C	$(1-\alpha)^n$	$[1-(1-\alpha)^{1-n}]/(1-n)$
Nucleation and nuclei growth[b]			
Mampel unimolecular law	A1	$1-\alpha$	$-\ln(1-\alpha)$
Two-dimensional growth	A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Three-dimensional growth	A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
Prout–Thompkins branching nuclei	A4	$\alpha(1-\alpha)$	$\ln[\alpha/(1-\alpha)]$
Diffusion[b]			
Parabolic law	D1	α^{-1}	$\alpha^2/2$
Valensi equation	D2	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
Jander equation	D3	$3(1-\alpha)^{1/3}/2[(1-\alpha)^{-1/3}-1]$	$[1-(1-\alpha)^{1/3}]^2$
Brounshtein–Ginstling equation	D4	$3/2[(1-\alpha)^{-1/3}-1]$	$1-2/3\alpha-(1-\alpha)^{2/3}$
Phase-boundary movement[b]			
One-dimensional	R1	Constant	α
Two-dimensional	R2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
Three-dimensional	R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$

[a] Ref. 10.

[b] Ref. 11.

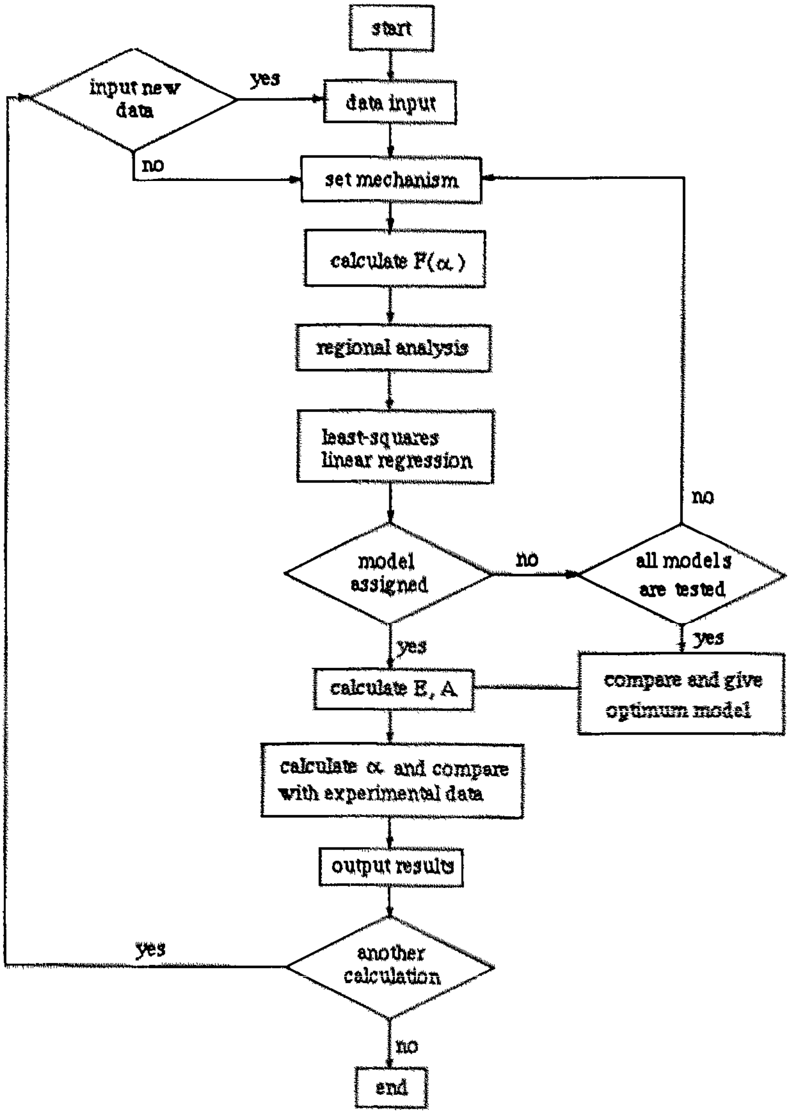

Fig. 1. Simplified block diagram of KNIS.

in Table 1. Three procedures are currently available for the selection of the relevant reaction mechanism.

(1) The model is assigned by the user.

(2) The best fit model is chosen by the system according to the optimum linearity.

(3) All possible models are applied and the corresponding results are printed out.

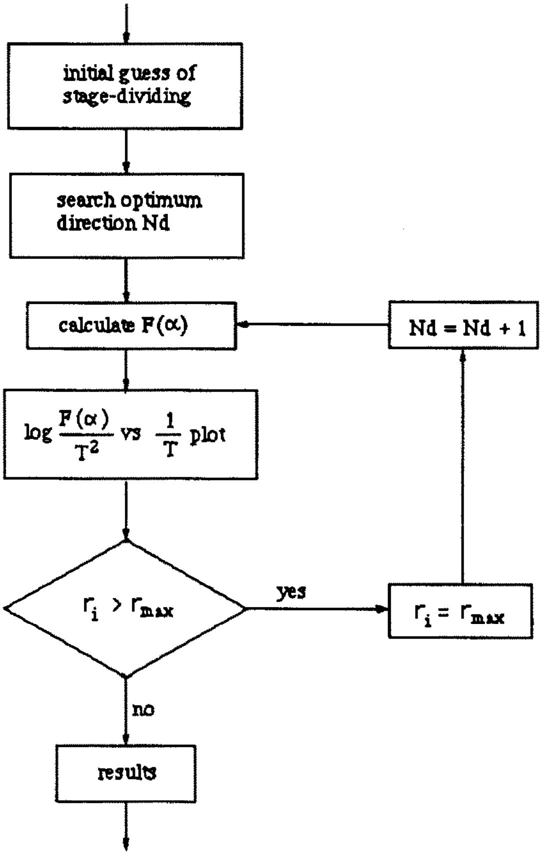

Fig. 2. Block diagram of STAGE-OPT programs for regional analysis.

The KNIS program provides flexible methods for the regional kinetic analysis of the entire data set, which at present include:

(1) $\alpha - T$ regions defined by the user;

(2) $\alpha - T$ regions defined automatically by the system. The "best fit" is given by the maximum linearity of each region.

The different stages of a reaction may be described by identical mechanisms or by different mechanisms. The automatic regional analysis is performed by the STAGE-OPT subroutine which incorporates a routine of general least-squares linear regression as shown in Fig. 2. An initial guess for the regions is made to commence the iterative loop. The linearity of each $\log[F(\alpha)/T^2]$ vs. $1/T$ plot is examined systematically over each region. Subsequently, new $\alpha - T$ regions are nominated. The iterative loop is continued until the maximum linearity of $\log[F(\alpha)/T^2]$ vs. $1/T$ for each of the regions is found.

A typical procedure for a KNIS run is as follows.

(1) The data input mode, "interactive" or "file-input", is selected.

(2) If the interactive mode is chosen, the experimental data are entered, otherwise the program reads the data from the data file indicated by the user.

(3) The relevant α–T regions, described by identical mechanisms or by different mechanisms, are established.

(4) The kinetic model selected is entered. If the mode of "assigned model" is selected, the subsequent calculations are based directly on that model; otherwise all kinetic models in the bank are tested, and the results generated are compared. Output of all results is optional.

(5) The regional analysis mode, "the stages of reaction are divided by the user" or "the stages of reaction are divided by the system", is selected.

(6) The linearity of $\log[F(\alpha)/T^2]$ vs. $1/T$ plots, as obtained by defined strategies, are tested.

(7) The relevant activation energies and pre-exponential factors are calculated.

(8) Based on the kinetic parameters obtained, the values of α are calculated and compared with corresponding experimental values.

(9) Output of results is generated.

KNIS is designed for users having little prior computer knowledge. A menu format is available in the user interface which organizes the alternatives into a simple yet effective progression of choice. The program is therefore easy to use.

APPLICATION OF THE PROGRAM

In order to test the KNIS program, the kinetic parameters from TG data for the decomposition of calcium oxalate monohydrate were derived. The KNIS program was also applied to the kinetic analysis of coal pyrolysis. The corresponding TG data were obtained using a Rigaku–Denki Type 8085 (Thermoflex) TG–DTA thermal analysis system, with the following experimental conditions: atmosphere, nitrogen; flow rate, 0.1 $\mathrm{dm^3\ min^{-1}}$; heating rate, 10 °C $\mathrm{min^{-1}}$; temperature range, 20–950 °C; crucible, platinum; sample mass range, 10–15 mg.

Decomposition of calcium oxalate monohydrate

It is well known that $CaC_2O_4 \cdot H_2O$ decomposes thermally in three stages:

I $\quad CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O$

II $\quad CaC_2O_4 \rightarrow CaCO_3 + CO$

III $\quad CaCO_3 \rightarrow CaO + CO_2$

The activation energy values for each stage as derived from the corresponding TG data (Table 2) are listed in Table 3. The activation energy values

TABLE 2

Values of α as a function of T, as derived from TG data for the thermal decomposition of $CaC_2O_4 \cdot H_2O$ in N_2

Reaction I		Reaction II		Reaction III	
T (°C)	α	T (°C)	α	T (°C)	α
157	0.196	449	0.045	687	0.119
161	0.255	454	0.057	695	0.150
165	0.327	457	0.068	701	0.180
168	0.400	462	0.085	707	0.212
172	0.495	466	0.098	714	0.265
177	0.600	470	0.121	719	0.301
181	0.724	475	0.160	722	0.340
		479	0.200	726	0.379
		482	0.257	729	0.425
		485	0.323	734	0.464
		490	0.389	741	0.573
		494	0.479	745	0.626
		497	0.615	749	0.680
		501	0.740	753	0.736
		505	0.845	757	0.788
		510	0.926	760	0.839
				765	0.885
				768	0.933
				772	0.967

derived by other authors [12–17] are also summarized in Table 3. The activation energy for reaction I is in the range 86–113 kJ mol^{-1}, 96–356 kJ mol^{-1} for reaction II and 163–227 kJ mol^{-1} for reaction III. In the present work, it was found that the "best fit" for the TG data obtained is with the Coats–Redfern model [10], with reaction orders of 1, 0.33 and 0.4 for reactions I, II and III respectively. The activation energy values obtained are 111 kJ mol^{-1}, 255 kJ mol^{-1} and 231 kJ mol^{-1} for reactions I, II and III respectively. These results agree well with corresponding literature data.

Pyrolysis of some Australian coals

The KNIS program has been applied successfully to the derivation of the kinetic parameters for the pyrolysis of a suite of brown coal samples and bituminous coal maceral concentrates. These coals exhibit two well-defined pyrolysis stages. The "best fit" criterion for both stages corresponds with the three-dimensional diffusion model D_3. The activation energy obtained for brown coal is in the range 80–84 kJ mol^{-1} for the primary pyrolysis, and 19–21 kJ mol^{-1} for the secondary pyrolysis. The activation energies of bituminous coals are 111–168 and 18–35 kJ mol^{-1} for the primary and secondary stage respectively. It is also found that a linear relationship exists

TABLE 3

Activation energy (E) data for the thermal decomposition of $CaC_2O_4 \cdot H_2O$

Author(s)	Method	Mechanism (Table 1)	Reaction I		Reaction II		Reaction III	
			n	E (kJ mol^{-1})	n	E (kJ mol^{-1})	n	E (kJ mol^{-1})
Coats and Redfern [10]	TG	C	0.71	90	0.38	259	0.46	216
Freeman and Carroll [12]	TG		1	92	0.7	310	0.4	163
Gurrieri et al. [13]	DTG			88		308		171
Liu et al. [14]	TG	C	1	86	0.7	273	0.4	225
Wendlandt [15]	DTA			113		356		
Fatu [16]	DTA			89				180
Gadalla [17]	TG	R3, A3, R3		117, 46 [a]		96		227
	TG	R3, A3, R3		126, 42 [a]		126		197
This work	TG	C	1	111	1/3	256	0.4	231

[a] From a two linear-segment "best-fit" analysis.

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* EVALUATION OF KINETIC PARAMETERS OF NON-ISOTHERMAL *
*              THERMAL ANALYSIS SYSTEM              *
*                      V1.0                         *
************************************************


SAMPLE: MORWELL COAL: HEATING RATE 10 C/MIN.

6. Diffusion: Jander equation
                      1/3 2
      F(a) = [ 1 - ( 1 - a )]

 Activation energy and pre-exponential factor
-----------------------------------------------
Model T1-T2    a1-a2   E(kJ/mol)A(1/sec.)    Rf
-----------------------------------------------
 6  278-474 0.05-0.53   79.67  0.680E+2  0.9992
 6  474-830 0.53-0.93   21.06  0.208E-2  0.9988
-----------------------------------------------

    Weighted mean activation energy =    46.44

    The errors of values of reaction fraction calculated
    by the models compared with experimental data are:

        average error        =   0.007
        standard deviation   =   0.010
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Fig. 3. An example of data analysis output.

between the weighted mean apparent activation energy and specific energy of the coal samples investigated. An example of the data output for the pyrolysis of Morwell brown coal is given in Fig. 3. The detailed results obtained from this study have been reported elsewhere [18].

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