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KINETIC EVALUATION OF NON-ISOTHERMAL THERMOANALYTICAL CURVES IN THE CASE OF INDEPENDENT THERMAL REACTIONS

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ABSTRACT

A least squares curve-fitting method was developed for the following thermoanalytical problem: "Find the kinetic parameters and the unknown initial amounts of the reactants from non-isothermal thermoanalytical curves in the case of two or more independent or quasi-independent thermal reactions". From a numerical point of view this problem differs from the non-linear least squares techniques used in other areas of reaction kinetics. The special difficulties which have arisen in such calculations were eliminated by parameter transformations and by separating the linear and non-linear parts of the problem. The method can be applied at any $T(t)$ functions. Thermoanalytical curves differing in temperature program can be evaluated simultaneously.

INTRODUCTION

In this paper those non-isothermal thermoanalytical examinations where the measured effect is produced by independent or approximately independent reactions will be considered.

Let x_j be the reacted mole fraction of the jth reaction and let us suppose that each reaction satisfies a kinetic equation of the following form

$$\mathrm{d}x_j/\mathrm{d}t = k_j(T)f_j(x_j) \tag{1}$$

where $k_j(T)$ is the rate constant and $f_j(x_j)$ is an arbitrary continuous function. (For f_j functions see, e.g., ref. 1 or 2). Let $\mathrm{X}(t)$ and $\mathrm{DX}(t)$ stand for thermoanalytical curves of integral and differential type, respectively. For the commonly used thermoanalytical techniques $\mathrm{X}(t)$ and $\mathrm{DX}(t)$ depend linearly on x_j or $\mathrm{d}x_j/\mathrm{d}t$

$$\mathrm{X}(t) = \sum c_j\, x_j(t) \tag{2}$$

$$\mathrm{DX}(t) = \sum c_j\, \mathrm{d}x_j/\mathrm{d}t \tag{3}$$

Here, coefficients c_j are the initial quantities of the reactants multiplied by such factors as the reaction heat (if DX = DSC), or the molecular weight of the volatile product (if X = TG). In many important practical problems the c_j coefficients are unknown and the primary aim of the thermoanalytical investigations is their determination. Other unknown parameters are the A_j pre-exponential factors and the E_j activation energies.

The $f_j(x_j)$ functions may also contain unknown parameters, e.g., when they are formally approximated by a power function

$$f_j(x_j) = (1 - x_j)^{n_j} \tag{4}$$

Equation (4) is frequently used with unknown n_j in such cases when the geometry of the reaction surface is too complex to derive f_j theoretically.

If the reactions considerably overlap, the thermoanalytical curves do not provide experimental x_j or dx_j/dt functions. Thus the c_j values cannot be read directly from the curves and the kinetic parameters cannot be determined by the methods used in the kinetic analysis of single reactions. In this case least squares curve-fitting should be applied to find the kinetic and c_j parameters.

PRELIMINARY DISCUSSION

Let X^{obs}, DX^{obs}, X^{calc} and DX^{calc} stand for the observed and calculated thermoanalytical curves. We shall look for those parameters at which either

$$S_X = \sum [X^{obs}(t_i) - X^{calc}(t_i)]^2 \tag{5}$$

or

$$S_{DX} = \sum [DX^{obs}(t_i) - DX^{calc}(t_i)]^2 \tag{6}$$

is minimal.

In this minimization the following problems arise.

(i) The S_X and S_{DX} surfaces are non-convex and frequently have physically meaningless partial minima. Thus the computation method should be constructed in such a way that the user could easily find good initial values for the unknown parameters.

(ii) During the minimization the true minimum can be reached through narrow, slightly curved valleys on the S_X or S_{DX} multidimensional surfaces. This fact makes the minimization difficult, since the direction of the steps should be chosen extremely carefully. However, this problem can be easily eliminated by proper parameter transformations. Without these transformations minimizations (5) and (6) can hardly be carried out, even in the single reaction case.

Besides the above aspects, partial attention should be paid to keeping the complexity of the computer program within acceptable limits. Thus it is worth using simple, direct search methods in the minimization to avoid gradient determination or multidimensional interpolation problems. In consequence of the high performance of the present computers, simple direct search techniques may be quite suitable for handling complex least squares problems[3, 4].

A SUITABLE COMPUTATIONAL SCHEME

The approximative solution of eqn. (1) can be easily obtained at any given set of kinetic parameters. The variables are separable and the $\int k_j(T)\mathrm{d}t$ integrals can be easily evaluated at any $T(t)$. At any given set of $x_j(t)$ or $\mathrm{d}x_j/\mathrm{d}t$, curves S_X and S_DX are linear functions of parameters c_j. This fact suggests the following computational scheme.

Let vector $\boldsymbol{p}$ denote the kinetic parameters. The computation starts at some initial $\boldsymbol{p}$ vector. Equation (1) is solved to obtain the corresponding $x_j(\boldsymbol{p}, t)$ or $\mathrm{d}x_j(\boldsymbol{p},t)/\mathrm{d}t$ $x_j(\boldsymbol{p}, t)$ functions. Using the linear least squares method we find those c_j values at which

$$S_\mathrm{X}(\boldsymbol{p}) = \sum_i [\mathrm{X}^\mathrm{obs}(t_i) - \sum_j c_j x_j(\boldsymbol{p}, t_i)]^2 \tag{7}$$

or

$$S_\mathrm{DX}(\boldsymbol{p}) = \sum_i \left[\mathrm{DX}^\mathrm{obs}(t_i) - \sum_j c_j \frac{\mathrm{d}}{\mathrm{d}t} x_j(\boldsymbol{p}, t_i)\right]^2 \tag{8}$$

is minimal. We change $\boldsymbol{p}$ systematically by a suitable algorithm and choose that $\boldsymbol{p}$ at which the minimization by parameters c_j gives the smallest S_X or S_DX value. This method has the following advantages:

(i) the number of unknowns in the non-linear least squares minimization is smaller;

(ii) there is no need for initial c_j values.

Similar computational schemes are frequently used in the numerical analysis.

TRANSFORMATION OF THE KINETIC PARAMETERS (I)

In this section those cases when the $f_j(x_j)$ functions do not contain unknown parameters will be considered. For the sake of simplicity we shall speak about the "peaks" of the thermoanalytical curves, although the proposed formulae are also valid for integral thermoanalytical curves.

Roughly speaking, at given $f_j(x_j)$, E_j and A_j define together the position and the width of the jth calculated curve. Through parameters c_j we choose the heights of the peaks to be optimal at each set of the A_j and E_j parameters.

Test calculations have shown that the finding of the optimal positions and widths of the peaks becomes relatively simple and efficient if we apply a parameter transformation which provides for each peak:

(i) a parameter shifting the peak left or right without changing its width; and

(ii) a parameter changing the width of the peak without affecting its position.

Let x'_j be a certain fixed value, say 0.5, and let t'_j be the time at which $x_j(t) = x'_j$. t'_j will be the parameter which defines the position of the jth peak. At given t'_j the energy of activation defines the width of the peak: smaller E_j values represent wider peaks and higher E_j values represent narrower peaks. Thus the second parameter will be E_j. At given t'_j and E_j, the corresponding A_j can be determined through the following form of eqn. (1)

$$A_j = \int_0^{x_j'} \frac{\mathrm{d}x}{f_j} \Big/ \int_0^{t_j'} \mathrm{e}^{-E_j/RT}\,\mathrm{d}t \tag{9}$$

In the following part of this section the question of the initial parameter values will be considered briefly. Having some practice in such calculations, good initial t'_j values can be estimated simply by the eye. If somebody prefers reading the position of the peak maxima on the measured curves, then such x'_j values should be chosen which correspond to the peak maxima. Here the results of Horowitz and Metzger[5] and Gyulai and Greenhow[6] can be applied. However, in the case of non-linear $T(t)$ or a sophisticated $f_j(x_j)$ function, the relationships between the position of the peak maximum and the corresponding kinetic parameters may become hopelessly sophisticated. In this case the choice of the x'_j values depends on the user's experience, intuition and taste. As regards the initial E_j values, it is worth underlining that too low E_j values may result in highly merged peaks and from this the program can converge to false minima. If the user prefers a geometrical characterization of the peak width rather than giving initial E_j estimations, then the transformation described in the following section may be used.

TRANSFORMATION OF THE KINETIC PARAMETERS (II)

In this section those cases when each of the $f_j(x_j)$ functions may contain an unknown parameter will be considered. Let us denote these parameters by n_j. If eqn. (4) is used, n_j are the formal reaction orders.

Let x''_j and x'_j ($x''_j < x'_j$) be some fixed values of x_j, for example, 0.3 and 0.6, and let t''_j and t'_j be the corresponding time values. As before, t'_j will be used to characterize the position of the peak. However, in this case E_j cannot define alone the width of the peak at fixed t'_j. Thus a more direct characterization of the peak width, the $\Delta t_j = t'_j - t''_j$ difference, will be chosen as the second parameter. Roughly speaking, a third independent parameter can affect only the degree of asymmetry of the peak at fixed t'_j and Δt_j. For convenience n_j will be chosen as the third independent parameter.

At given t'_j, Δt_j and n_j, the corresponding A_j and E_j values can be determined in the following way. Let $g_j(x_j)$ and $I_j(t)$ stand for integrals

$$\int_0^{x_j} \mathrm{d}x_j/f_j \text{ and } \int_0^{t} \mathrm{e}^{-E_j/RT}\,\mathrm{d}t,$$

respectively, and let us write eqn. (1) in the following form

$$g_j(x_j) = A_j\, I_j\,(t) \tag{10}$$

Hence, $g_j(x'_j) = A_j\, I_j(t'_j)$, $g_j(x''_j) = A_j\, I_j(t''_j)$ and

$$g_j(x'_j)/g_j(x''_j) = I_j(t'_j)/I_j(t''_j) \tag{11}$$

At linear $T(t)$, $I_j(t)$ is a product of $e^{-E_j/RT}$ with a nearly-constant factor, thus eqn. (11) can be written in the form[7]

$$\ln \frac{g_j(x'_j)}{g_j(x''_j)} \cong \frac{E_j}{R}\left(\frac{1}{T''_j} - \frac{1}{T'_j}\right) \tag{12}$$

Here $T'_j = T(t'_j)$ and $T''_j = T(t''_j)$. At hyperbolic $T(t)$ eqn. (12) becomes exact.

At other types of $T(t)$, eqn. (11) should be solved numerically. Note that I_j depends on E_j roughly exponentially at any $T(t)$, thus it is worth solving the logarithmic form of eqn. (11). Having E_j on hand, A_j can be obtained through eqn. (9). The transformation of A_j and E_j into t_J and Δt_j can also be used at fixed n_j values. In this case the minimization by the t'_j and Δt_j parameters is practically equivalent to that by the t'_j and E_j parameters. To illustrate this let us rearrange eqn. (12) using the $d(1/T) = -dT/T^2$ relation

$$T_j^2 \ln \frac{g_j(x'_j)}{g_j(x''_j)} \cong E_j\,(T'_j - T''_j) \tag{13}$$

Here T_j is the average of T'_j and T''_j. Equation (13) shows that at linear or hyperbolic $T(t)$ and fixed n_j, E_j is inversely proportional to Δt_j.

LEAST SQUARES EVALUATION OF MORE THAN ONE THERMOANALYTICAL CURVE

During the kinetic evaluation, three to four parameters (c_j, A_j, E_j and, if any, n_j) should be determined for each reaction. However, if the overlap is too strong, one thermoanalytical curve might not contain sufficient information for the determination of these parameters. In other words, it may arise that several parameter sets provide equally good fit between the calculated and the observed curves. If this problem emerges, more thermoanalytical curves should be involved in the calculations.

These thermoanalytical curves may differ in the initial concentration of the reactants as well as in the temperature program. If the thermoanalytical curves in consideration have the same $T(t)$, their simultaneous evaluation may be carried out by the same method as that for the single ones. At different temperature programs the following treatment can be applied.

Let m stand for the serial number of the measurements. We look for those c_j, A_j, E_j and, if any, n_j, which minimize one of the following sums

$$S_X = \sum_m \sum_i [X_m^{obs}(t_i) - X_m^{calc}(t_i)]^2 \tag{14}$$

$$S_{DX} = \sum_m \sum_i [DX_m^{obs}(t_i) - DX_m^{calc}(t_i)]^2 \tag{15}$$

(The terms in eqns. (14) and (15) may be multiplied by suitable weight factors). As before, the c_j parameters can be determined by the linear least squares method for any set of kinetic parameters. At fixed $f_j(x_j)$ functions the position of a peak at two different temperature programs defines the corresponding A_j and E_j. This immediately suggests that in the non-linear least squares minimization the peak positions would be varied directly instead of A_j and E_j. Let I and II stand for two different temperature programs. Let x_j^{I} and x_j^{II} be some fixed values and let $x_j(t_j^{\mathrm{I}}) = x_j^{\mathrm{I}}$ at temperature program I and $x_j(t_j^{\mathrm{II}}) = x_j^{\mathrm{II}}$ at temperature program II. The t_j^{I} and t_j^{II} values which characterize the position of the jth peak at two different temperature programs will be used in the non-linear least squares minimization instead of the A_j and E_j values. At fixed $f_j(x_j)$ they define E_j and A_j through the following equations

$$g_j(x_j^{\mathrm{I}})/g_j(x_j^{\mathrm{II}}) = I_j^{\mathrm{I}}(t_j^{\mathrm{I}})/I_j^{\mathrm{II}}(t_j^{\mathrm{II}}) \tag{16}$$

$$A_j = g_j(x_j^{\mathrm{I}})/I_j^{\mathrm{I}}(t_j^{\mathrm{I}}) \tag{17}$$

Here the superscripts on I_j indicate the $T(t)$ function at which the integration is carried out.

At linear temperature programs eqn. (16) may be simplified in the same way as eqn. (11) (see, e.g., ref. 7).

$$\ln \frac{a^{\mathrm{I}} g_j(x_j^{\mathrm{I}})}{a^{\mathrm{II}} g_j(x_j^{\mathrm{II}})} \cong \frac{E_j}{R} \left(\frac{1}{T_j^{\mathrm{II}}} - \frac{1}{T_j^{\mathrm{I}}} \right) \tag{18}$$

Here a^{I} and a^{II} denote the heating rates. At hyperbolic temperature programs eqn. (18) becomes exact. At other types of $T(t)$ the logarithm of eqn. (16) should be solved numerically.

The $(A_j, E_j) \rightarrow (t_j^{\mathrm{I}}, t_j^{\mathrm{II}})$ transformation has also proved useful at unknown n_j.

PROGRAMMING

The following three parts of the calculation can be carried out by commonly available "library" subprograms:

(i) the solution of the logarithmic form of eqn. (11) or (16) in case of general $T(t)$ functions;

(ii) the linear least squares determination of the c_j parameters and the calculation of the corresponding S values;

(iii) the minimization in the non-linear least squares method.

Note that the solution of eqn. (1) can also be carried out by a Runge Kutta or predictor-corrector subprogram. However, in the case of linear or hyperbolic $T(t)$ it is more economic to compute the solution directly from the equation

$$x_j = g_j^{-1}[A_j I_j(t)] \tag{19}$$

where g_j^{-1} stands for the inverse function of g_j. Formulae suitable for the high precision calculation of integrals $I_j(t)$ have been treated in a previous paper[8]. Equation (19) may also be useful at general $T(t)$ functions.

In this way the programming is relatively simple and the resulting program can be run on minicomputers of 64 K bytes of total memory. With careful programming the required memory can be diminished below 32 K bytes and the computation can be carried out on "desk-top computers". For example, if we use a library subprogram, or the modification of a library subprogram, for the linear least squares determination of the c_j parameters, then the matrix of the $x_j(t_i)$ or $\mathrm{d}x_j(t_i)/\mathrm{d}t$ values should be stored until the calculation of the c_j values. The storage of these matrices can be avoided if the coefficients of the normal equations are determined simultaneously with the $c_j(t_i)$ or $\mathrm{d}x_j(t_i)/\mathrm{d}t$ values, and if S is computed from the normal equations and the obtained c_j values.

NUMERICAL EXAMPLES

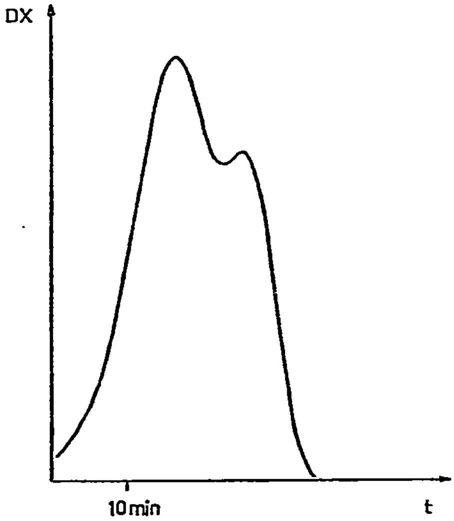
Two hypothetical thermoanalytical curves (curves I and II) were constructed and evaluated. They differed only in the heating program.

Two independent reactions were considered:

$E_1 = 35$ kcal mole^{-1} $\quad$ $E_2 = 40$ kcal mole^{-1}
$A_1 = 4.90 \times 10^{12}$ min^{-1} $\quad$ $A_2 = 3.88 \times 10^{13}$ min^{-1}
$n_1 = 1$ $\quad$ $n_2 = 1$
$c_1 = 50$ $\quad$ $c_2 = 50$

These parameters were chosen in such a way that at a usual linear heating program a DX curve should consist of highly overlapping peaks.

To calculate curve I a linear $T(t)$ with a heating rate of 4° min^{-1} (temperature program I) was used. The resulting DX curve is shown in Fig. 1.



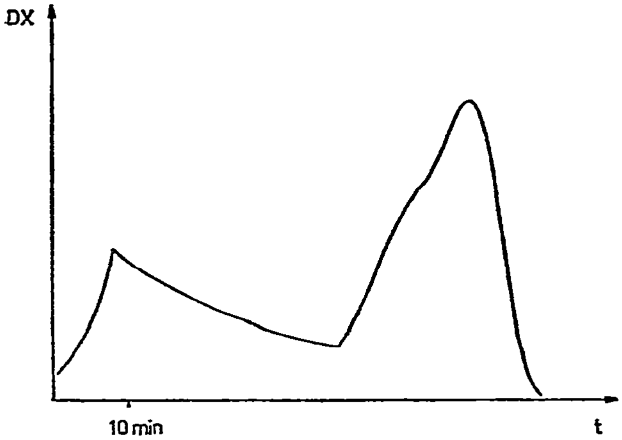


Fig. 1. DX curve at heating program I between 240 and 380°C.

Fig. 2. DX curve at heating program II between 240 and 380°C.

A DX curve of a rather different shape can be obtained by inserting an isotherm section in the temperature program. Thus temperature program II was constructed in the following way

(i) linear heating with 4° $\min^{-1}$ rate up to 270°C;

(ii) an isotherm section of 30 min at 270°C;

(iii) linear heating with 4° $\min^{-1}$ rate up to the end of the degradation.

At 270°C reaction 1 has about 12 times higher rate than reaction 2. Thus the majority of reactant 1 gives out in the isotherm section while the amount of reactant 2 practically does not change here. The resulting DX curve (curve II) is shown in Fig. 2.

For the evaluation of the curves, DX(t_i) values were taken every 30th second between 240 and 380°C.

Since real thermoanalytical curves always have experimental errors, random numbers of Gaussian distribution were added to the DX(t_i) values. The deviation of the random numbers was 0.05. This value corresponds to 1.75 and 3.25% relative deviation at curves I and II, respectively. (The average DX value is about half at curve II than at curve I, see Figs. 1 and 2). When the curves were evaluated simultaneously, the calculations were repeated with double greater deviation.

The simulated DX(t_i) data were evaluated in the following calculations:

(i) finding A_j, E_j and c_j (j = 1,2) at fixed n_j by the separate evaluation of curves I and II;

(ii) finding A_j, E_j and c_j at fixed n_j by the simultaneous evaluation of curves I and II;

(iii) finding A_j, E_j, n_j and c_j by the separate evaluation of curves I and II;

(iv) finding A_j, E_j, n_j and c_j by the simultaneous evaluation of curves I and II.

The results are shown in the Table 1. The first two columns refer to the temperature program and the simulated measurement errors of the evaluated curves. The other columns contain the error of the obtained parameters. It can be seen that the precision of the obtained parameters is slightly better at curve I than at curve II. This

TABLE 1

THE ERRORS OF THE OBTAINED PARAMETERS

Each row corresponds to a separate calculation. The first column indicates the curves evaluated in the given calculation: the second column shows the deviation of the simulated measurement errors; the other columns contain the absolute values of the errors of the parameters.

$T(t)$	σ	δn	$\delta \log A$	δE	δc
I	0.05	—	0.13	0.16	0.6
II	0.05	—	0.20	0.50	0.6
I + II	0.05	—	0.06	0.17	0.08
I + II	0.10	—	0.12	0.30	0.08
I	0.05	0.03	0.50	1.37	1.8
II	0.05	0.04	0.55	1.57	3.3
I + II	0.10	0.03	0.33	0.88	1.6

fact seems surprising since temperature program II provides far better resolution for the two reactions. (The first half of the curve is dominated by reaction 1, while the second half of the curve is dominated by reaction 2). However, the average height of curve II is smaller than that of curve I, and in this way the simulated errors have higher relative deviation (3.25%). However, temperature programs of this type may have great importance in checking whether the examined reactions are really independent. For example, in the case of competitive reactions inserting the isotherm section would have considerably diminished the size of the second peak in Fig. 2.

The calculations were carried out on a CDC 3300 computer. The computing time varied between 1 and 5 min. Considering the relatively low speed of the applied computer (an old, second generation type) these times seem reasonable. The obtained fits were good. The obtained mean square deviations differed only slightly from the mean square deviation of the simulated errors. By choosing deliberately wrong initial values for the parameters, false minima and very bad fits could also have been obtained.

APPLICATIONS

The kinetic evaluation method presented here has been developed over a period of two years. During this time about 140 DSC, TG and TG–MS curves were evaluated in this way, mainly in industrial research. The majority of these calculations belong to the DSC examination of metallic alloys. The corresponding results will be published soon. Another topic of application was the thermal analysis of surfaces in catalytic research.

LIST OF SYMBOLS

a	heating rate
A_j	pre-exponential factor
c_j	a factor associated with the initial concentration of reactant j.
$\mathrm{DX}(t)$	a thermoanalytical curve of differential or derivative type (DSC, DTG, MTA)
E_j	energy of activation
$f_j(x_j)$	the conversion depending part of the rate equation
$g_j(x_j)$	$\int_0^{x_j} \mathrm{d}x_j/f_j$
g_j^{-1}	the inverse function of g_j
$I_j(t)$	$\int_0^{t} \mathrm{e}^{-E_j/RT}\,\mathrm{d}t$

$k_j(T)$	rate constant
n_j	any unknown parameter in $f_j(x_j)$
p	the vector of the kinetic parameters
S, S_X, S_{DX}	least squares sums
t and T	the time and the temperature
x_j	reacted mole fraction of reactant j
X(t)	a thermoanalytical curve of integral type (e.g. TG)

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