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ANALYSIS OF DTA CURVES AND CALCULATION OF KINETIC DATA USING COMPUTER TECHNIQUE

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ABSTRACT

Principles of two computer programs useful for the evaluation of heterogeneous kinetics are described.

The first program ALANTA allows to obtain the non-isothermal kinetic curve from the shape of general DTA peak using the DTA-equation derived elsewhere[1].

The second program SQUEST determines the kinetic mechanism which is the most appropriate to a given non-isothermal kinetic curve and evaluates the corresponding kinetic parameters. The program decides between 19 kinetic models and uses both integral and differential methods of evaluation.

INTRODUCTION

Methods of thermal analysis associated with the indication of enthalpy changes become one of the most important sources of information on the behaviour of solid materials[1]. The quality of such information depends on high level of instrumentation and evaluation of experimental curves.

One of the most utilized methods is that of differential thermal analysis (DTA). The transformation of recorded quantity, ΔT, to the desired information about the property of the system is understood as the analysis of an experimentally obtained DTA curve. For this it is necessary to use principles describing relations between the recorded quantity, experimental conditions and properties of the system. The final relation can be called the "DTA equation" which was derived and discussed in our previous works[2-5], in which we also analysed the actual meaning of individual terms.

The complicated form of the DTA equation can be expressed as[1]:

$$\dot{a} = K_{\mathrm{DTA}}\left(\Delta T - \dot{\Delta}T\frac{Cp}{K_{\mathrm{DTA}}}\right)\Big/\Delta h \qquad (1)$$

where a is the degree of conversion, K_{DTA} is a temperature dependent apparatus constant, C_p is the heat capacity, Δh is heat production of the process and superposed dots mean the time derivative. The entire analysis of DTA curve consists of the transformation of the experimentally measured dependence $\Delta T = \mathrm{f}(t)$ (and/or $= \mathrm{f}(T)$, (where t and T are time and temperature, respectively) to the time dependence of the degree of conversion $a = \mathrm{f}(t)$ (possibly its time derivative $\dot{a} = \mathrm{f}(t)$).

Kinetic data of simple processes are determined from the dependence of the rate of process upon the parameters defining the state of the system, usually in the form[6]

$$\dot{a} = k(T)\mathrm{f}(a), \tag{2}$$

where $k(T)$ is the temperature-dependent kinetic rate constant and $\mathrm{f}(a)$ is a function expressing the instantaneous phase composition of the system. Kinetic appraisal of the process thus represents the determination of the rate constant $k(T)$ and simultaneous estimation of the mathematical form of the $\mathrm{f}(a)$ function.

EVALUATION OF DTA CURVES

The DTA curve is a graphical or numerical record of measured quantity, ΔT, on time-dependent variables characterizing external conditions, usually the temperature of the surroundings. Curves consist of the regions of monotonous course (base-lines) and of the regions where the enthalpy change yields effects disturbing the monotous course of the curve. Most often effect is called peak which is characterized[7] in Fig. 1 (original and final baseline – temperature differences BLO and BLF, respectively, peak beginning and peak end temperatures TO and TF, resp., extra-

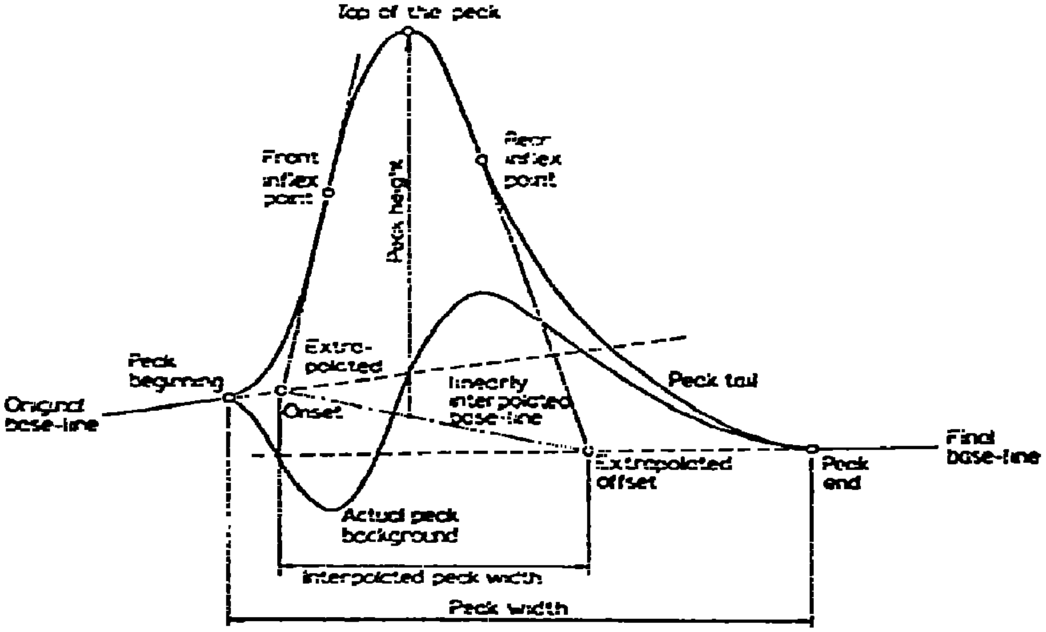

Fig. 1. Basic characteristics for DTA peak description.

polated onset and offset temperatures TON and TFN resp., and rear inflex point temperature TIF).

For the entire analysis of the DTA peak, the program ALANTA (ALgorithm for the ANalysis of TA curves) was compiled[7]. The algorithm utilizes two basic subroutines EXIN and DGT3 which produce interpolation and numerical derivation. The flowchart of ALANTA was given in ref. 7 and the program covers 18000 bites.

Input data are sorted into four groups:

(1) Data characterizing experimental arrangement as temperature dependence of thermocouple EMF, apparatus constant and heat capacities of holders; in the form of tables.

(2) Data describing sample (specification, weight of sample, thermal capacity, mole weight) and recording (sensitivity of ΔT and T measurements, chart speed).

(3) Data of characteristic points of DTA peak.

(4) Specification of DTA peak in the form of non-equidistant sequences of x- and y-coordinates in millimeters.

All data are converted into seconds and Kelvins. The temperature of individual points is established by linear interpolation while the thermal capacities and apparatus constants are assigned by quadratic interpolation.

The basic calorimetric relation can be read in the FORTRAN language as follows:

$$\begin{aligned} \mathrm{DTA} = {} & \mathrm{DK/AC} - (\mathrm{CO} + \mathrm{ALFA} * \mathrm{DC} - \mathrm{CR}) * \mathrm{FI/AC} - \\ & - (\mathrm{CO} + \mathrm{ALFA} * \mathrm{DC}) * \mathrm{DDT/AC} - \mathrm{DH} * \mathrm{DALF/AC}, \end{aligned} \tag{3}$$

where DTA is the temperature difference between the sample (S) reference (R), and DDT its time derivative, DK is the difference of heat transfer coefficients, CO and CR are heat capacities of the sample and reference including their holders, DC is the heat capacity change due to the process, ALFA is the degree of conversion and DALF its time derivative, FI is the heating rate, AC is the apparatus constant and DH is the enthalpy change due to the process.

For the initial state of the sample before the peak, ALFA = 0, DALF = 0 and DDT is constant, so that it follows[8] from eqn (3):

$$\mathrm{BLO} = \mathrm{DK/AC} - (\mathrm{CO} - \mathrm{CR}) * \mathrm{FI/AC} - \mathrm{CO} * \mathrm{DDT/AC}, \tag{4}$$

where BLO means the original baseline (linearly extrapolated for $T > \mathrm{TO}$). Similarly, we can obtain the equation for the final baseline BLF (linearly extrapolated for $T <$ TF), in

$$\mathrm{BLF} = \mathrm{DK/AC} - (\mathrm{CO} - \mathrm{CR} + \mathrm{DC}) * \mathrm{FI/AC} - (\mathrm{CO} + \mathrm{DC}) * \mathrm{DDT/AC}, \tag{5}$$

if considering conditions of the final state of the sample (ALFA = 1, DALF = 0 and DDT = const.).

By comparing eqns (4) and (5), we can describe the thermal capacity change during the process as

$$\mathrm{DC} = \mathrm{AC} * (\mathrm{BLF} - \mathrm{BLO})/(\mathrm{FI} + \mathrm{DDT}). \tag{6}$$

Linear interpolation of the baseline in the region of $(\mathrm{TO} < T < \mathrm{TF}) - \mathrm{BL}$, is made as a linear combination of BLO and BLF

$$\mathrm{BL} = (1 - \mathrm{ALFA}) * \mathrm{BLO} + \mathrm{ALFA} * \mathrm{BLF} \tag{7}$$

This procedure is in accordance with the ICTA recommendation if ALFA fulfils the following requirements:
$\mathrm{ALFA} = 0$ for $T < \mathrm{TON}$
$\mathrm{ALFA} = (T - \mathrm{TON})/(\mathrm{TFN} - \mathrm{TON})$ for $\mathrm{TON} < T < \mathrm{TFN}$
$\mathrm{ALFA} = 1$ for $T < \mathrm{TFN}$

The initial peak area (ARO) is treated in accordance with the ICTA recommendation for the peak area evaluation and is calculated by the numerical integration of the difference (DTA − BL) within the limits from TO to TF.

$$\mathrm{ARO} = \int_{\mathrm{TO}}^{\mathrm{TF}} (\mathrm{DTA} - \mathrm{BL})\mathrm{d}T \tag{8}$$

Entire values of ALFA for individual temperatures are then given by

$$\mathrm{ALFA} = \frac{1}{\mathrm{ARO}} \int_{\mathrm{TO}}^{T} (\mathrm{DTA} - \mathrm{BL})\mathrm{d}T \tag{9}$$

The sum of the first three terms of eqn (3) is called the actual peak background, BG, and can be calculated with the equation[7,8]:

$$\mathrm{BG} = \mathrm{BL} - (\mathrm{CO} + \mathrm{ALFA} * \mathrm{DC}) * \mathrm{DDT}/\mathrm{AC}, \tag{10}$$

where BL is obtained by substitution of ALFA from eqn (9) into the eqn (7).

The final (true) peak area, FARO, is then calculated by the numerical integration of (DTA − BG) within the limits from TO to TF, or

$$\mathrm{FARO} = \int_{\mathrm{TO}}^{\mathrm{TF}} (\mathrm{DTA} - \mathrm{BG})\mathrm{d}T \tag{11}$$

The refined (true) degree of conversion is consequently found for individual temperatures as

$$\mathrm{ALFA} = \frac{1}{\mathrm{FARO}} \int_{\mathrm{TO}}^{T} (\mathrm{DTA} - \mathrm{BG})\,\mathrm{d}T \tag{12}$$

The final values of FARO and ALFA are elaborated by successive iteration loop of eqns (7), (10), (11) and (12) which is completed when two consecutive values of FARO agree within 1 %. This is usually reached within three loops.

Print out lists following data for both linear and actual peak background approximation:

measured quantity DTA and its derivative DDT
degree of conversion and its derivative DALF
peak background BL or BG
change of the heat capacity during the process DCP
enthalpy change during the process DH.

EVALUATION OF KINETIC PARAMETERS

By kinetic parameters we understand constants, which substituted into a chosen kinetic model, agree with the experimental kinetic curve (the time-dependence of the degree of conversion). For the description of mechanism of solid-state reactions the simple two- and three-dimensional model of reacting particles is used as illustrated in Fig. 2. The program utilizes nineteen preselected types of heterogeneous processes^{6,9} and ten different reactions orders for homogeneous-like processes.

Entire analysis utilizes computer program SQEST^{9} of an extent of 70000 bites

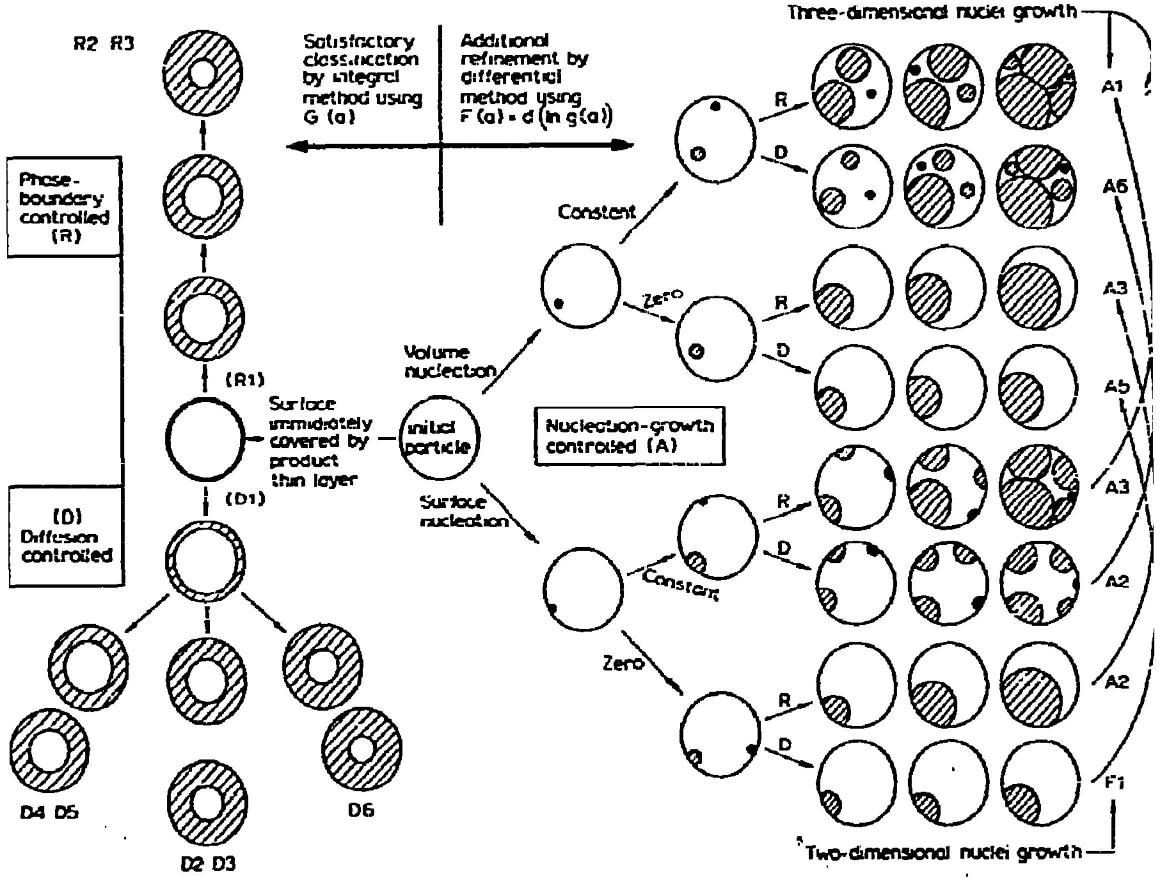

Fig. 2. Graphical illustration of computer classification of solid-state processes.

which employs two basic subroutines PX and PLOT assuring the evaluation of the function $p(x)$[10] and numerical print of graphs[9, 11].

Input data are divided into two groups:

(1) Data characterising the input kinetic curve (number of points, length of step, heating rate, onset temperature, and desired accuracy of evaluation).

(2) Entire values of ALFA vs. time-dependence.

The basic integral method of evaluation[9] starts from mere ALFA vs. T data using the equation:

$$\mathrm{CI} = \mathrm{ALOG(GALFA)} - \mathrm{ALOG(PX)} \tag{13}$$

where CI is a quantity which should be constant in the case of a satisfactory choice of a kinetic model relation $f(a)$, ALOG means natural logarithm, GALFA is the so-called integral form of the function $f(a)$

$$\left(\text{defined as } g(a) = \int_{a} \mathrm{d}a / f(a)\right)$$

and PX is the temperature-dependent function called exponential-integral[10]. Algorithm tests the constantness of CI for functions GALFA corresponding to various kinetic models. Kinetic parameters for individual models are then calculated through a modified Arrhenius plot: (log $g(a)$ vs. $1/T$).

The standard deviations of given plots are also calculated together with the corresponding extent of the linearity region.

For the case that the integral method is not sensitive enough to distinguish various forms of the function GALFA (when merely differing by the value of the exponent[9]), the program provides a consequent procedure[11] which uses more sensitive but less accurate evaluation by the differential method. This algorithm classifies the processes according to the extent of the linearity region in which the plot of $\log(\dot{x}/f(x))$ vs. $1/T$ is linear in order to assist further refinement of nucleation-growth models. It yields only a complementary graphical print of most probable functions $f(x)$.

Resulting data provide maximum information concerning the more probable mechanisms while excluding less probable ones between the 19 employed kinetic models. Final classification of so far acceptable mechanisms is made separately for three chosen regions of process which makes it possible to determine the change in reaction mechanism during the process. Apart from the extent of the linearity region, the model relations are classified according to the value of the re-exponential factor.

The print-out includes the mechanism specification (diffusion D, phase-boundary reaction R and nucleation-growth A), values of associated activation energy and pre-exponential factor accompanied by the standard deviation and the extent of linearity. Graphical printing of the plot GALFA vs. $1/T$ is also available together with the complementary plot according to the differential method of kinetic data evaluation[11].

TABLE 1

RESULTING KINETIC DATA FOR THE PHASE TRANSFORMATION OF $BaCO_3$

	ΔH *(deg. sec.)*	E *(kcal)*	Z	*Mechanism*	*Linearity region (%)*
Linear background	613	87.5 118	10^{15} $2 \cdot 10^{21}$	A1 A3	54
Actual background	617	38 52	$1.5 \cdot 10^{[illegible]}$ $8.5 \cdot 10^{6}$	A1 A3	51

EXAMPLE FOR THE PROGRAM APPLICATION

To demonstrate our procedure for the evaluation of the DTA peak, the phase transition of $BaCO_3$ at 810 °C was chosen. The measurement was carried out on DTA apparatus by Netzsch. The measuring head was equipped by the differential Pt–Pt/Rh10 thermocouple. The thermoelectric power difference was registered with a chart sensitivity 0.05 mV/250 mm at a chart speed equal 1200 mm h^{-1}. The heating rate was 5 K min^{-1}.

The results are listed in Table 1. The first line gives the data obtained considering $\dot{\alpha}$ to be proportional to DTA – BL (eqn (9)) using the linearly interpolated baseline BL, while the following line shows the corresponding data calculated by proportional to DTA – BG (eqn (12)) using ALANTA.

From Table 1, we can see that the type of rate-controlling process remains unchanged while the values of activation energy and frequency factor are fundamentally changed. It is evident that the applied correction to the experimentally obtained DTA curve considerably affects the values of evaluated kinetic data. In our case, the activation energy changes by about 25% which exceeds the normally accepted error of about 10%. This demonstrates very well the necessity of utilization of the non-simplified DTA equation (eqn (3)) in order to obtain the information on the rate of the process and the associated kinetic data.

DISCUSSION

The above described computer procedures make it possible to apply DTA corrections and carry out a more complex fitting of hypothetical models with the corrected (kinetic) DTA curve. This was impossible by normal treatment. All this is certainly a starting point for the solution of additional questions which are necessary for a more advanced evaluation of DTA measurements[5, 14].

Program ALANTA works with the DTA equation which assumes the homogeneous distribution of temperature within the sample which is invalid particularly for solid materials. This was demonstrated on the rectangular probing pulses[12] generated by a microheater in the DTA sample holder, where the correction was not found satisfactory[4, 13] in the region of beginning of the peak and the end of the peak.

Program SQUEST is based on mathematical treatment developed for normal handling of TG curves. This procedure assumes certain simplifications. The investigated process is so simple that the instantaneous state of the sample is characterized by a single parameter a. The rate of process $\dot{a}$ is then a function of two variables a and T, i.e., $\dot{a} = f(a, T)$. This function is then replaced by the multiple of two separate functions each of them depending only on a single parameter, see eqn (2). For the analytical description of $f(a)$, the kinetic models deirved for isothermal conditions are usually employed. Recently, the validity of some of these models was also approved for non-isothermal conditions[14]. The function $K(T)$ is expressed by means of an exponential in accordance with the practice of chemical statistics. This, however, does not include the effect of a stability of the initial state on the course of reaction nor the effect of equilibrium temperature[15-18].

Another more general problem is the reliability of the calculated kinetic data. If resulting data are expected to have a true physical meaning, the program should only be applied to experimentally well-distinguished cases. Possible inhomogeneity of resulting data, e.g., an impossible type of mechanism selected by the program, large values of standard deviation or inconstancy of kinetic parameters, may be a signal of an inadequate application of the above evaluation procedure for the description of some more complex solid-state reactions. In accordance with the use of computers for fitting the hypothetical kinetic models to an experimental kinetic curve we face the problem of selecting certain criteria to describe the suitability of these models. Principles of mathematical statistics should be more generally applied which, of course, will bring along additional problems concerning the transformation of the experimental kinetic curve into the form of a mathematical record[11, 15].

The present possibility of computer analysis certainly offers more sophisticated computer programming which will be able to include more general kinetic models suitable for the description of, e.g., melting or dissociation of solid solutions, spinodal decompositions or other phase separations in multicomponent systems, where a single conversion parameter a is not sufficient to describe the instantaneous state of multiparameter processes[16, 17].

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