

Recommendations for computer-aided data extraction and model search in homogeneous non-isothermal reaction kinetics

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(Received 15 July 1991)

Abstract

Detailed procedures for the kinetic evaluation and interpretation of thermoanalytical experiments are proposed in order to determine the mechanistic concentration code, which is an efficient tool for data extraction in homogeneous reaction kinetics. The representation includes aspects of decision theory and is complemented by the experimental conditions and mathematical expressions needed for suitable computer software.

The description is aimed at (1) the direct determination of the best-fitted one-step or two-step models, (2) the determination of their evidence factors and the (often apparent) activation data, (3) suggestions for three- and four-step models by distinguishing low and high concentration ranges, and (4) the comparison of the validity of presumed five-step or multistep mechanisms. The concepts refer to non-isothermal kinetics, but may also be used for isothermal kinetics; extrapolation to solid phase is also possible.

1. INTRODUCTION

Because of the chaotic evolution of data processing, the problem of data extraction following a thermoanalytical, time-resolved experiment becomes more and more important [1–5]. Software for evaluation and interpretation of thermoanalytic records is therefore required to produce as much data as necessary, but not to confuse the user by the appearance of data on the screen which he does not need (but perhaps the computer does) [6].

Consequently, the procedures proposed in this paper will follow a clear but perhaps unusual path that is indicated by the general concept of kinetics in order to determine the best model for an observed composite reaction; however, reliable procedural proposals undoubtedly have to be based on the grounds of probability and statistics theory. The validity of the

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

expressions and the utility of the procedures presented here will not be discussed because they have been the subjects of a number of publications [7]. Nevertheless, some remarks are appropriate at this stage.

It is now possible to produce theoretical TA plots with negligible error in fractions of a second, starting from one model for the reaction and another for the apparatus. Reference strategies, which have always been essential for the construction of twin arrangements for TA, must improve the evaluation procedures because the direct comparison of an experimental reaction plot with a theoretical plot using the same tools should strengthen the validity of an interpretation by suppressing the effects of unavoidable, arbitrary procedural fixations, e.g. the concept of overall reaction. Then the principle of pattern recognition in its broadest sense can be applied to generate a distribution list of all models to be compared, ordered with respect to their probabilities. The number of these models may be significantly reduced by defining a reference reactant and a reference reaction [8].

Furthermore, because mathematical expressions in non-isothermal kinetics are even more complicated than in isothermal kinetics, e.g. the exponential integral, it is not possible in most cases to use expressions that are both exact and explicit for calculating the various data; iterative procedures have to be used instead, and status elements are often preferred over rather nonsensical numerical data. Only those expressions that are directly needed for the proposed evaluation strategy will be discussed [9].

Finally, the equipment used must be tested to ensure that it meets with the requirements of the mathematical tools, reviewed here. The most adequate apparatus is an “all-liquid” type [10,11], fitted with a stirring system and a temperature tracer inside the sample, preferably a solution. However, many commercial instruments also provide calibration functions for solid state processes, so that an apparatus may account for the effect of the physical constants in order to obtain such fundamental kinetic data as the ideal kinetic half-width and the shape index.

2. EVALUATION OF KINETIC CURVES

2.1. *General; role of DTA*

The kinetic records considered should be based on linearly progressing time and on a derivative form, which is achieved, i.e. in power-compensating DSC or DTG by considering the rate directly. They may be obtained from primary on-line files of 1500–3000 points (around 1 s^{-1} for a heating rate of $m = 1.5 \text{ K min}^{-1}$) [12,13], after smoothing, e.g. by a Sawitzky–Gohlay algorithm [14], and subsequent data restriction to 120–150 points ($2\text{--}3 \text{ min}^{-1}$). For methods where transport processes modify the observed kinetics, as in DTA or heat-flux DSC, there is no proportionality between the

rate of a partial process and its contribution to the signal; this is also the case for UV reaction spectroscopy outside the limits of the Lambert–Beer law. For DTA, two methods may be mentioned for treating the computer plot assuming at first a one-step process; these methods may be similarly applied to other techniques influenced by transport kinetics.

(a) In a stepwise (forward or backward) progressing evaluation procedure, the temporary rate constant for temperature T is obtained directly from eqns. (1) and (2) below [10], using the fitted difference ratio (see Section 2.4) instead of the derivative $d\theta/dt$:

$$n = 1 \quad k(T) = \frac{(\kappa/C_p)\theta + d\theta/dt}{\int_t^\infty (\kappa/C_p)\theta dt - \theta} \approx \frac{c\theta + d\theta/dt}{c \int_t^\infty \theta dt - \theta} \quad (c = \kappa/C_p) \quad (1)$$

(first order) or

$$n = 2 \quad k(T) \approx \frac{V \Delta H}{C_p} \frac{c\theta + d\theta/dt}{\left[c \int_t^\infty \theta dt - \theta \right] \left[([A]_0 - [B]_0)(V \Delta H/C_p) + c \int_t^\infty \theta dt - \theta \right]} \quad (2)$$

(second order) where k is the rate constant, V the volume of sample, c the kinetic cell constant (time^{-1}), θ , the temperature difference sample/reference, t the time, ΔH the enthalpy of reaction, C_p the heat capacity of the sample, $[A]_0$ and $[B]_0$ the starting concentrations of reactants for a reaction $A + B = \text{product(s)}$; and κ the heat conduction coefficient.

(b) The rate is obtained similarly, but first using the Tian–Calvet (Newton) differential equation

$$v = \frac{C_p}{V \Delta H} \left(\frac{d\theta}{dt} - c(T)\theta \right) \quad (3)$$

where v is the reaction rate.

The subsequent evaluation is the same as for the rate curves (see Section 2.4 below).

2.2. Problem of subdivision

The records may consist of several overlapping peaks. At first glance, it seems reasonable to divide the records into sections when the peaks are sufficiently separated from each other. However, because there is then no direct knowledge of the temporary concentrations of the reactants or transients after the first section, an analogous “calibrated” evaluation of

the second section is impossible: the type of starting reaction and concentrations (reference reaction and reference reactant) for the remaining part are unknown. Therefore one should try to consider additional peaks as distortions of the main peak if ever possible.

2.3. Problems of baseline and further preparation of the plot

With a view to the expected kinetic information, the estimation of the baseline between the onset and end of the signal requires an extrapolation from both limiting straight lines, similar to a calorimeter plot. Steps or breaks in the connecting or the interior parts of the baseline have to be avoided. A simple simulation of the baseline is provided by a function that transforms smoothly the initial straight line into an exponential function, characteristic even for kinetic heat-decay processes:

$$v(t) = a\{1 - \exp[+b(t - t_0)]\} \quad (4)$$

At least three points are needed to obtain the parameters a and b . A better, but rather complicated equation, also considering a final linear asymptote, is

$$v(t) = m_1(t - t_0) \exp[-b_1(t - t_0)^{p_1}] + (m_2t + n_2) \exp[b_2(t - t_0)^{p_2}] \quad (5)$$

where b_1 and b_2 depend on the parameters of the two asymptotic straight lines, i.e. the slopes m_1 , m_2 and the absolute ordinate n_2 . Usually, $p_2 = p_1$ may be assumed. Equation (4) is preferred if the baseline falls off in the last part, e.g. because of a strong temperature dependence of the cell constant.

Another often useful form of the baseline is known from calorimetry: its vertical shift can be assumed as being proportional to the contribution of the respective area to the total area [15]. This procedure starts from any initial baseline and is improved by a repetitive calculation over the total curve. Nevertheless, there are cases where instead of convergence, a fluctuation between two baselines occurs; furthermore, this kind of baseline also depends on the usually unknown kinetic scheme. This main problem cannot be totally eliminated. It is therefore recommended that evaluations are restricted to systems where the changes in the total heat capacity are nearly negligible with respect to the changes caused by chemical kinetics. However, if the same baseline procedures are used for both experimental and theoretical plots, the uncertainties must be strongly reduced.

After smoothing of the plot (120–150 equidistant points per section are recommended) and subtraction of the baseline, the next data needed are the maximum peak height and the corresponding peak temperature; these allow for later elimination of the heat feedback responsible for deviations from a linearly increasing sample temperature, and for an approximate

calculation of the reaction enthalpy from the calorimetric measurements. After input of the temperatures for onset, peak and end (if the temperature is not recorded in a second plot), these data may be obtained in a pre-loop, passing all stored points of the plot.

2.4. Rate constants of the reference reaction

The next step is the calculation of the temporary rate constant of an assumed, but fitted reference reaction, which depends on the actual reaction temperature. The procedure is different for rate-proportional curves and DTA curves (see Section 2.1).

In the first case, the ordinate value is divided by the signal parameter in order to obtain the actual rate; then the rate, integral (which in the ideal case should be identical with the concentration of the deficient reactant) and derivative are used for calculating the rate coefficient, corresponding to the actual temperature $T(t)$; if there is no separate temperature plot, $T(t)$ can be estimated from the time and heating rate, corrected by the heat feedback. Then the rate coefficient is

$$n = 1 \quad k(T) = \frac{[A]_0 - \int_t^\infty [A(t)] dt}{[A(t)]} \quad (6)$$

(first order)

$$n = 2 \text{ and } [A]_0 = [B]_0 \quad k(T) = \frac{[A]_0 - \int_t^\infty [A(t)] dt}{[A(t)]^2} \quad (7)$$

$$n = 2 \text{ and } [A]_0 \neq [B]_0 \quad k(T) = \frac{[A]_0 - \int_t^\infty [A(t)] dt}{[A] \left([B]_0 - [A]_0 + \int_t^\infty [A(t)] dt \right)} \quad (8)$$

For DTA curves, the derivative of the ordinate is also used (eqns. (1) and (2)). In general, the simple difference ratio should not be formed from two points of the temporary time interval; rather 3–5 points of the plot should be used for obtaining the integral, i.e. the Taylor fit, and the derivative by special interpolation and extrapolation procedures [14]. For orders different from unity, the rate coefficient k has to be corrected after the calculation of the total reaction enthalpy (see eqn. (2)).

It is simplest to determine the slopes of inflection and the two half-value times in this loop (see Section 2.7) and to test the linearity of the heating rate of the reference sample by checking whether the ratios $(T_m - T_0)/$

$(t_m - t_o)$ and $(T_e - T_m)/(t_e - t_m)$ are equal; the temperatures T (at onset, maximum and end) are corrected by subtraction of the respective heat feedback effects.

In the last part of the signal curve (highest temperatures), the use of eqn. (1) often leads to negative, nonsensical values of the rate constants. If this is observed in an interval, the whole remaining part of the plot must be blocked for the k determination, which must be considered in a recommended weighting procedure [13].

2.5. Area and standardization of the kinetic data

For a rate curve, the total area is identical with the reacted portion of the deficient reactant. However, for equilibria or an otherwise incomplete reaction, or if the signal parameter is unknown, areas different from $[A]_0$ are obtained. In order to reach a direct comparison with the conditions in theoretical runs for the different models, it is practical to repeat the evaluation after a respective modification of the signal parameter (equal to the proportionality coefficient), so that the area/ $[A]_0$ ratio becomes unity.

For a DTA curve, such a standardization is unnecessary because the rate constant is obtained by involving the enthalpy as a standardizing signal parameter, which here is a “byproduct” of the kinetic study; the enthalpy is available from the area, heat capacity, volume, cell constant and starting concentration of the deficient reactant.

2.6. Activation parameters of the reference reaction

The calculation of the activation energy is based on an Arrhenius straight-line fit of $\log k$ versus $1/T$, i.e. for rate curves

$$E = R \frac{T_1 T_2}{T_2 - T_1} \ln \frac{v_2}{v_1} \quad (9)$$

for DTA curves

$$E = R \frac{T_1 T_2}{T_2 - T_1} \ln \frac{c\theta_2 + (d\theta/dt)_2}{c\theta_1 + (d\theta/dt)_1} \quad (10)$$

obtained by usual least-squares programs. The corresponding A factor is

$$k_\infty = k(T) \exp(E/RT) \quad (11)$$

Four sets of such activation data should be determined (completed by graphic inspection of the fits [16]) for a unimolecular or bimolecular one-step reaction, and with respect to the initial data (25% of the total time range is recommended) or overall data, using an appropriate weight-

ing procedure. The activation parameters are true data only if the mechanistic coordinates indicate an elementary process (see Sections 2.7 and 2.8). They are needed for obtaining these general kinetic coordinates, after having corrected the half-width h and the shape index S using the specific time, and then calculating the reaction-type index M .

2.7. Half-width and shape index

Beginning at the onset, there are some special situations in the main evaluation loop, as many as seven for the simplest case of an elementary process: the onset (when the ordinate is equal to a reference level, referred to the maximum, e.g. 0.5%); the first half-width point; the first point of inflection; the maximum of the plot; the second point of inflection; the second half-width point; and the end of the curve (see the first situation). These all correspond to characteristic times and temperatures of kinetic interest. The second point of inflection and the second half-width point are sometimes barely separable or are inverted in their sequence, especially for DTA curves which are quasi-linear in their second part for certain cell constants. Hence, it is often difficult to estimate the points of inflection unambiguously, which is also the case for the more fluctuating rate curves. However, because it has been shown that the slopes at both half-width points also reflect the asymmetry of the curve, it is better to make a compromise: one should fit two straight lines over greater ranges of the plot (around 7% of the total time interval each), the first covering the expected first point of inflection ($uk = (3 - \sqrt{5})/2$ for first order and $2(2 - \sqrt{3})/[A]_0$ for second order [17]), and the second around the mean of the second half-width and inflection point. The nearly invariant nature of the slope ratio (equal to the shape index S [18–20]) is not lost by this change. For DTA curves, a corrective left-shift of the first point, reciprocal to the cell constant, improves the accuracy of the left slope.

The estimation of the half-width as the difference between two temperatures causes far fewer problems, although the error (as also for M) is, in the most unfavourable case of a first-order reaction around 0.24 per number of points, which may reach approx. 1% for the recommended approx. 130 points per file. However, increasing the scheduled number of points causes increasing errors in the integration procedure because the area contributions are reduced too much.

2.8. Specific times and correction procedures

The specific time u_m , referring to the peak maximum, eliminates the influence of the activation data on the shape of the curve [21–25]. For a bimolecular reference process, the shape also depends on the initial concentrations of the reactants, $[A]_0$ and $[B]_0$.

At first, the first-order value is calculated [26–28] in an iterative loop, using the equation

$$u_m(1, n+1) = \frac{E_1(\log e)^2}{Rm[F_1 + \log u_m(1, n)]^2} \quad (12)$$

where $e = 2.71828\dots$, F_1 is the log A factor, E_1 the activation energy of the unimolecular reference reaction, m the heating rate, R the gas constant and $u_m(1, \text{start}) \approx 10/m$.

The loop can be closed if $u_m(n)/u_m(n-1) < 0.001$, which is generally fulfilled after 3–4 turns. The “bimolecular” u value is obtained from $u_m(1)$; thus, for $[A]_0 = [B]_0$

$$u_m(2) = \frac{E_2(\log e)^2}{Rm[F_2 + \log u_m(1) + \log[A]_0]^2} \quad (13)$$

For $[A]_0 < [B]_0$, an additional, usually rapidly converging iterative procedure can be used [29,30]:

$$(uk)_m(n+1) = \frac{1}{[B]_0 - [A]_0} \frac{([B]_0/[A]_0)Z_m - 1}{([B]_0/[A]_0)Z_m + 1} - (uk)_m(n) \quad (14)$$

using

$$Z_m = \exp([(A]_0 - [B]_0)(uk)_m] \quad (15)$$

and starting with

$$(uk)_0 = 1/([B]_0 - [A]_0) \quad (16)$$

$u_m(2)$ is then obtained:

$$u_m(2) = \frac{E_2(\log e)^2}{Rm[F_2 + \log u_m(1) - \log(uk)_m]^2} \quad (17)$$

The “kinetic coordinates” S and M should correspond to an ideal “rate curve”, i.e. no heat feedback: the reaction temperature should increase linearly with time. Therefore the necessary correction for the hitherto obtained rough data for half-width h and shape index S depends on the maximum signal height θ_m , referred to the specific temperature difference mu_m , and for DTA, in addition, on the kinetic cell constant c (dimension, time^{-1}).

For the unimolecular case, the following semiempirical correction expressions are proposed for DTA curves (“ uc theory” [26,29,31]):

$$h_\infty(1) = \frac{h_{\text{exp}} + [h_{\text{exp}} - (m/c) \ln 2][a_3 + a_5 \ln(uc)]\theta_m/(mu)}{1 + [a_1/(u + a_2)]uc} \quad (18)$$

where $u = u_m(1)$ and the empirical constants are for an “all-liquid” type of apparatus which, for $0.1 < m < 10 \text{ K min}^{-1}$, are $a_1 = 3.45$, $a_2 = 11$, $a_4 = 0.36$, $a_5 = 0.03$, and also

$$a_3 = \frac{a_4 + a_5 \ln(uc)}{u} \approx \frac{a_4}{u} \quad (19)$$

For the ideal shape index

$$S_\infty(1) = S_{\text{exp}} \frac{(uc)^{b_1 + b_3 \theta_m}}{[(uc)^{b_1} + b_2] [1 + (b_5 + b_6 uc) \theta_m / (mu)]} \quad (20)$$

using $b_1 = 1.25$, $b_2 = 0.44$, $b_3 = 0.13 \text{ m/u}$, $b_5 = 0.27$ and $b_6 = 0.105$. For a second-order process

$$h_\infty(2) = \frac{[h_{\text{exp}} - (m/c) \ln 2] \{ [a_1 / (a_2 + u)] \theta_m \} + h_{\text{exp}}}{1 + a_3 (uc)^{-a_4}} \quad (21)$$

using, similarly, $a_1 = 0.7$, $a_2 = 2.3$, $a_3 = 0.19$, $a_4 = 1.1$, and

$$S_\infty(2) = \frac{S_{\text{exp}}}{1 + b_3 (\sqrt{m}/u) \theta_m} \frac{(uc)^2}{(uc)^2 + (b_1 - b_2 u) u} \quad (22)$$

using $b_1 = 0.0375$, $b_2 = 0.00138$ and $b_3 = 0.058$.

For a non-equimolecular concentration ratio of the reactants, $q = [B]_0/[A]_0$, a plausible formulation is a linear superposition of the values for first and second order (eqns. (18), (19), (21) and (22)) using the ratio parameter

$$f(\text{AB}) = \ln \frac{e(q-1) + 1 + d}{q + d} \quad (23)$$

where $e = 2.71828\dots$, and $d = 0.6$; and a ratio f_M , obtained from eqn. (17)

$$f_M = \left(\frac{F_2 + \log u_m}{F_2 + \log u_m - \log(uk)_m} \right)^2 \quad (24)$$

thus leading to

$$h_\infty(\text{AB}) = h_\infty(1) f(\text{AB}) = h_\infty(2) [1 - f(\text{AB})] f_M \quad (25)$$

and

$$S_\infty(\text{AB}) = S_\infty(1) f(\text{AB}) + S_\infty(2) [1 - f(\text{AB})] \quad (26)$$

Although eqns. (25) and (26) are very approximate for complex kinetics, because a linear superposition is only justified for the n th-order case, they seem to be sufficiently accurate [30,32,33] because their errors represent corrections of corrections only; the reference character of the strategy must reduce them further.

In all these semiempirical equations (eqns. (18) and (20)–(22)), the coefficients $a \dots$, and $b \dots$ may be modified if another type of apparatus is used. Expressions for other techniques based on rate curves instead of DTA curves, such as power-compensating DSC, may be readily derived from our expressions using very high c values so that the thermal lag effect is negligible towards the heat-feedback effect, represented by the term $\theta_m/(\mu)$. Very strong feedbacks should be avoided in experiments because then the time resolution disappears owing to the approach to impulse kinetics [31].

2.9. Reaction-type index and molecularity (order)

Whilst the corrected S value may be used directly for the discussion of the model, the corrected half-width has to be referred to the obtained activation data of the reference reaction, using the specific time and leading to the reaction-type index

$$M(1, 2) = fu_m(1, 2)m/h_\infty(1, 2) \quad (27)$$

where f is the calibration factor equal to 0.0460 (if M is in $\text{kJ mol}^{-1} \text{K}^{-1}$), u_m is the u value for a presumed unimolecular or bimolecular reaction (see Section 2.8), m is the heating rate and h_∞ is the ideal half-width (see Section 2.8).

The “kinetic coordinates” S and M can be used to estimate two mathematical orders, namely

$$n_s \approx (0.9/S + 0.56)^{1.94} + 0.24 - 0.64S \quad (28)$$

and

$$n_M = (0.0195/M)^{1.94} \quad (29)$$

For $n_s < 0.4$, a better expression is [18]

$$n_s = 1.25\sqrt{S} \quad (30)$$

For an elementary unimolecular or bimolecular reaction using $[A]_0 = [B]_0$, both orders are equal and identical with the molecularity of one or two. In a bimolecular reaction using $[A]_0 \neq [B]_0$, both (apparent) “orders” are mostly between one and two. For complex reactions, the order may be encoded by the symbols 0, L (low order, < 1), 1, M (medium order, $1 < M < 2$), and 2, H (high order, > 2).

A further parameter reflects approximately whether a formal n th-order reaction holds:

$$I_{\text{mech}} = 23.9M(1 + 2S) \quad (31)$$

where $I_{\text{mech}} = 1$ for the formal n th-order reaction. However, if the starting

concentration of the deficient reactant is not in the range of unity, corrections are necessary [19,34] if n is also far from unity.

2.10. Further options

The M and S values may be compared with M/S regions stored in the computer which indicate the possible two-reaction models (TRMs) from only one experiment [32,35]. Thus, lists of possible TRMs may already be displayed at this stage. Although a more detailed study demands the study of series for the determination of the mechanistic concentration codes (MCCs, see Section 4), such lists are much more instructive than the correlation coefficients of the Arrhenius straight-line fits [16,36].

2.11. Storage of data

In the described evaluation loop, parameters are determined which should be stored, together with the restricted curve data, in a common data file (RDF) belonging to each experiment or simulation (situation flag). Thus the evaluation can be repeated by the use of other key parameters (see Section 3.1) or of another type of baseline if the RDF had been installed before the subtraction.

3. TREATING EXPERIMENTAL OR THEORETICAL SERIES

3.1. Important data

The important parameters belonging to an RDF are the following:

(a) Input data: date; filename (expressing number of species; varied species, substance class(es)); initial concentrations of components; solvent key number (for up to five parameters, expressing values and temperature dependence of heat decay (cell constant c) and C_p ; 100–150 y values; similarly, the respective times, if not equidistant; otherwise, the time interval for the progression; T values if also recorded; onset and final temperature; desired heating rate; switches for evaluating mode, flag for type of record (DTA or rate-proportional curve); reference flag, also used for correction; flag for unfavourable conditions (too high or too small a signal, poor temperature linearity).

(b) Output (resulting) data:

(b1) General: real average heating rate; maximum signal height; linearity of $T(t)$; peak temperature; onset, peak and final times; shape index (several for different modes) and half-width.

(b2) Energetics: total area in conversion/ $[A]_0$ or $^{\circ}\text{C} \times \text{min}$ (DTA); reaction enthalpy.

(b3) Kinetics: percentage of the total time interval ($t(\text{end}) - t(\text{onset})$) yielding a positive rate constant (two values for $n = 1$ and $n = 2$); activation energy, A factor, and correlation coefficient; specific time u (four values each: $n = 1$ or 2 , and initial or overall); corrected shape index and half-width; M index (four values); for $[A]_0 \neq [B]_0$, extrapolated S and M values also; mathematical orders n_S and n_M . For reactions in solution, an initial and overall prediagnosis is useful, together with a critical comment on $\log A$ ($\log A > 17$, chain reaction or autocatalysis?; $\log A < 5$, complex mechanism?).

In particular, the non-derivable parameters should be stored in the RMF.

3.2. Series-extracting files (SEFs)

Discussion of the kinetics requires a rapid survey of the response parameters as a function of the condition parameters. Therefore a series file should be created which contains the extracted information of all its RDFs (without the values of the record itself): first, the series name (which may classify the problem and may contain the encoded components used, and which of these were varied etc.) and the total number of runs. An SEF should include the particular plot-specific parameters, such as heating rate, reactant concentrations, reaction enthalpies (for DTA/DSC), maximum signal heights, onset, maximum and final temperatures and times, M and S values, and possibly the eight activation data, the four correlation coefficients of the Arrhenius diagram, both formal orders etc.

SEFs enable one to avoid storage problems on the computer if they are sufficient to determine the MCCs and other codes, because individual experimental and theoretical files may then be deleted.

3.3. Databanks

For all experimental and theoretical plots, separate libraries should be installed which may be further subdivided into smaller sections, combining the results for special types of reactant or model. Rapid call for particular files or series should be based on wild-card character inputs for the filenames, but also on parallel inputs for the limits of any parameter set. In this way, new series may be arranged under a given aspect, and such temporarily formed SEFs may be transferred to the command area where they may be used (see Sections 3.4 or 4) or stored in a series databank.

3.4. Graphic representation

A graphic check is very useful for studying various correlations, e.g. the compensation effect (is E a linear function of A ?), or the Kissinger

dependence of T_m on the heating rate. It is recommended that a logarithmic x scale be used because many kinetic functions are semilogarithmic; many response parameters should generally be studied as a function of the logarithm of the initial concentration (see the definition of pH). Furthermore, one should generate some auxiliary vertical or horizontal lines on the screen, for example for $[A]_0 = [B]_0$ in a bimolecular reaction, for $I_{mech} = 1$, for a correlation coefficient of unity or for the orders one and two in a representation of M or S versus the logarithmic concentration, or versus each other; this will facilitate the interpretation. A printer should be used for generating series sheets, also containing correlation figures for the most important parameters; thus, three semilogarithmic plots, $S-[A]_0$, $MX_0-[A]_0$ and $MX-[A_0]$ (reference order $X=1$ or 2) should always be created because the automatic determination of the mechanistic concentration code (MCC) may fail occasionally and has then to be replaced by a manual procedure.

4. DETERMINATION OF THE MECHANISTIC CONCENTRATION CODE

4.1. General

The S , M_0 and M values of the individual runs of a series, stored with their concentration values in the SEFs, allow for the determination of a special $3 \times N$ matrix, the MCC, which is the result of a data-extracting procedure (Fig. 1); its determination covers four stages (see Table 1): (1)

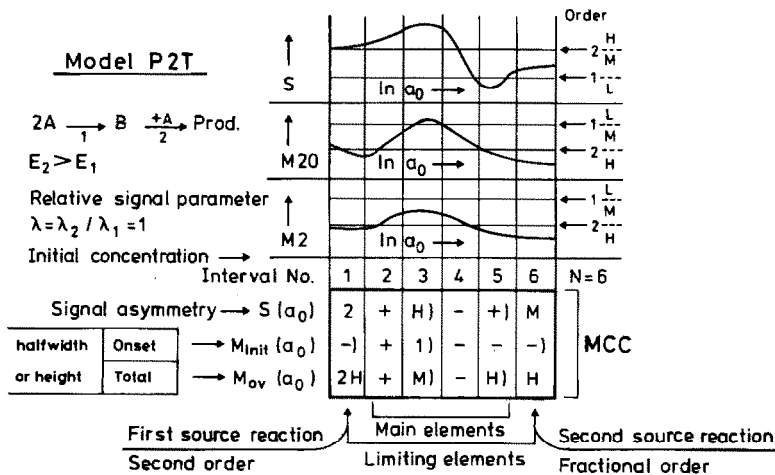


Fig. 1. Determination of the mechanistic concentration code (MCC) for the two-reaction model P2T: λ_i , signal parameter (proportionality coefficient) for the rate of step i ; a_0 , initial concentration of species A; N , number of intervals in the MCC (string length); L, 1, M, 2 and H, order or order range (see text).

TABLE 1

Some mechanistic concentration codes (MCC) of models containing a bimolecular step of type AB^a

AB	PAB1	PABT*	PABT	
A + B →	A $\xrightarrow{+B}$	A $\xrightarrow{+B}$ X $\xrightarrow{+A}$	same	
$\begin{array}{ c } \bullet \\ \hline \begin{array}{c} 1 + - 1 \\ 1 - + M \\ 1 - + 1 \end{array} \\ \hline \end{array}$	$\begin{array}{ c } \bullet \\ \hline \begin{array}{c} 1 + \uparrow - \backslash 1 \\ 1 - \downarrow + / M \\ 1 - + 1 \end{array} \\ \hline \end{array}$	$\begin{array}{ c } \bullet \\ \hline \begin{array}{c} 1 1) - \uparrow + - 1 \\ 1 1) +) + -) 1 L \\ 1 - - \downarrow + -) L \end{array} \\ \hline \end{array}$	$\begin{array}{ c } \bullet \\ \hline \begin{array}{c} 1 + + - M \\ 1 - C + + 1 \\ 1 - \downarrow + + M 1 \end{array} \\ \hline \end{array}$	$\begin{array}{ c } \bullet \\ \hline \begin{array}{c} 1) 1 + - - - 1) \\ 1 + + - -) + C \\ 1 +) - + -) + 1) \end{array} \\ \hline \end{array}$
N = 4	4	6	5	7
simplest mode	refined	refined	refined	refined
		$E_2 > E_1; \lambda_1 = \lambda_2$	$E_2 < E_1$	$E_2 > E_1$
<hr/>				
F2AB	POZ3/3 steps	POZ4A/4 steps		
A $\xrightarrow{+A}$ X $\xrightarrow{+B}$	A $\xrightarrow{+B}$ X $\xrightarrow{+A}$	A $\xrightarrow{+B}$ X $\xrightarrow{+X}$ Y →		
$\begin{array}{ c } \bullet \\ \hline \begin{array}{c} 2) -) + \uparrow ? - 2 \\ 2) +) - C) ? + 2 \\ 1 L +) - \downarrow +) + 1 \end{array} \\ \hline \end{array}$	$\begin{array}{ c } \bullet \\ \hline \begin{array}{c} 1 M + M + M - 1) - \uparrow - - 1 \\ 1) + - - H, H +) 2M \\ 1 + + L - - \downarrow + \uparrow -) \end{array} \\ \hline \end{array}$	$\begin{array}{ c } \bullet \\ \hline \begin{array}{c} 1 1 + 1M - + 1 + \downarrow - + M - -) \\ L) + - - H - H - H) +) - +) \\ L) + + L - - + M - + / - + / \end{array} \\ \hline \end{array}$		
N ≥ 7	N = 8	10		
refined mode	refined	refined		

^a •, 1:1 reactant concentration ratio; N, number of intervals (elements). Special element notations (see text): C, order depends on $\lambda_{rel} = \lambda_2 / \lambda_1$; ?, questionable; ↓, unsafe steep decrease to instability point.

subdivision of the total range of initial concentrations into *N* intervals, characterized by uniform behaviour; (2) fixation of the respective code symbols; (3) calculation of the order for the C intervals of parameter constancy (eqns. (28)–(30)); (4) special corrections, restrictions, or adding further symbols, as for instability effects or two-point intervals (indistinct information).

For a system of *q* reacting components, *q* – 1 MCCs usually include all the information on kinetic models.

4.2. Pre-estimation and optimization of the interval limits

Starting with the experiment with the lowest initial concentration, for every new point it has to be considered whether the type of behaviour, given by the points hitherto checked in this interval, has changed; in the simplest procedure, between constant (C) and variable (+ or –). In this case, this active interval has to be closed and a new interval opened, which usually accepts another element. (However, it may happen that the later points do not confirm this new behaviour.)

For a refined analysis, intermediate cases between constant and variable, such as indistinct constancy, (C), or indistinct variability, (+) or (–), are also distinguished. In every installed interval, the best-fitted straight line should be calculated for discussing their average slope with a view to certain barrier values, depending partially on the required tolerance level. Therefore an automatic iterative procedure needs, for a particular point n in the interval under consideration, the following operational periods.

(a) Calculate the slope of the approximate straight line (smooth slope) and, for $n = n^* + 1$ (n^* is the first point of the interval), calculate the direct slope for the second point, using $y(n) - y(n - 1)$.

(b) Check whether the difference $y(n) - y(n^*)$ is inside the tolerance level (yields C) or not (yields a variable type).

(c) If the interval is of variable type, the direct slope or, later on, the smooth slope is needed in order to decide between + and –.

(d) In the case of a C-type interval to be closed, a smooth average slope is needed to distinguish between +) and C etc.

(e) Compare the symbol with that of the previous run: if it is the same, close the interval and return to (a) for the next point ($n + 1$).

(f) If the closed interval has two points only, add] for the second space.

(g) Return to (a) for the next point ($n + 1$).

4.3. Fixing the final symbols

For each of the three parameters, the proposed interval limits may be partially different, especially between S and the group of M parameters ($M10$ and $M1$, or $M20$ and $M2$), which are rather similar. Because the MCC was defined using common interval limits for the three strings, the best concept found was taking the design of that string which shows the most intervals (elements) as the prototype for both the others; scheduling a common set for all parameters before using the optimizing algorithm will often result in an unmanageably high number of intervals.

4.4. Symbols for refinement and simplification of code strings

If the code determination is restricted to only one parameter, the case of two neighbouring and identical interval elements is not allowed; they have to be joined, and the interval length becomes $N - 1$.

An advantageous concept for rather refined codes is to define two-space elements for one interval, the first being the main element. For simplified considerations, the second symbol may be omitted. The following symbols seem adequate: first space: +, – or C; classified into 0, L, 1, M, 2 and H (see Section 2.9). Second space:) (indistinct),] (two points per interval only), +, or – (for a C-type first symbol), C or blank. Then, elements of the type CC, e.g. 1L, M2, indicate intermediate cases for the order, with a distinct approach to the order or order range due to the first symbol.

4.5. Extensions for instabilities

It is a special feature of certain kinetic models that concentration intervals with extremely steep slopes in S or M exist, signifying points of instability. This is generally the case if steps of the AB type (Table 1) are involved. A single AB reaction shows such a point at the 1:1 concentration barrier ($[A]_0 = [B]_0$), leading to the S string 1 + – 1 (simplified code). For the instabilities, the following symbols are proposed for the second space:

/, very steep increase; next interval: main element of C type;

\, very steep decrease; same;

↑, very steep increase; next interval: – or – \ element;

↓, very steep decrease; next interval: + or + / element.

Then, the AB reaction is characterized by the S string 1 + ↑ – \ 1; however, in rather complicated models, a sequence + ↑ – \ or – ↓ + / suggests the presence of such a step though the instability point may then be shifted away from the 1:1 barrier. The additional symbols for the second space are inserted after comparing the smooth average slope with two scheduled reference slopes in period (f) (see Section 4.2); these decide between such symbols as C +, +C, + and + /.

5. CREATING DISTRIBUTION LISTS FOR ALL TWO-REACTION MODELS

5.1. Abbreviations for the models

The two-reaction models (TRM) represent the simplest description of the peculiarities of complex homogeneous kinetics [7,37]; elementary reactions (formal one-step models) may be understood as degenerate TRMs. For defining an adequate model name, it is advantageous to establish a classifying sequence of three elements, the first and third being absent in elementary reactions.

(1) Main element, describing the type of coupling: P, parallel; F, consecutive, G, opposing (reversible); U, independent (uncoupled reactions).

(2) Index for the first reaction (for P or U types preferred at lower temperature); corresponds to the reference order: 1, first order; 2 or AB, second order; schemes $2A \rightarrow$ and $A + B \rightarrow$ (using $[A]_0 \neq [B]_0$).

(3) Index for the second reaction: analogous to first index.

Thus, FAB1 represents the reaction $A + B \rightarrow X \rightarrow \text{product(s)}$. Some further, special models such as cross-over or catalytic TRMs are described in refs. 7 and 38 (see Fig. 1).

5.2. *Databank for one- and two-step models*

The optimum MCCs were stored in a databank. They had been determined using a large-scale computer project [7,8,39] by varying the condition parameters (signal and activation parameters) independently of each other. MCCs differ considerably in their string length N ; whereas the elementary models 1 and 2 have $N = 1$, and AB or GAB1 have $N = 4$; all other TRMs have at least $N = 5$; and because of possible peak-splitting effects, especially for the F and U models, N can be up to 9. Consequently, the string length, although rarely estimated exactly, is a valuable parameter for kinetic pre-interpretation.

However, for all methods based on proportionality between derivative contribution and an individual rate for every step, the best way to determine the model is to compare the three strings of the MCC with the theoretical code set and to find the common shift for the best agreement. DTA plots can be included if obtained in all-liquid apparatus (see Sections 2.7–2.9).

5.3. *Restriction of models to be examined*

In order to reduce both the CPU times and the quantity of the data displayed, it is not necessary to compare all TRMs in the databank (which are approx. 50 because the cases $E1 > E2$ are distinguished from cases $E1 < E2$). Depending on the conditions of the experiments, the second element (first index) in the string for the model name (Section 5.1) may often be fixed: for one reacting component used, AB is not adequate as a reference process, and 2 (which signifies dimerization) is often less probable; conversely, for two or more components, 1 is inadequate as a reference order because the second component should react with the first. Furthermore, U types are often impossible, or they reflect undesired reactions of impurities of the reactants.

5.4. *Rating matrix*

The rating matrix summarizes the degree of agreement between a compared element of an experimental and a theoretical string; as a guide line, total agreement of the symbols must yield a rating of unity, total disagreement zero (excepting for symbols denoting uncertainty, such as M) or +) etc.). However, there are various possibilities inbetween. Both a simple and a refined matrix are described in refs. 7 and 38; an example of a

TABLE 2

Interpretation of different string lengths (N) and shifts (d) (see main text and eqn. (32))^a

Subject	$N_{\text{exp}} < N_{\text{theor}}$	$N_{\text{exp}} = N_{\text{theor}}$	$N_{\text{exp}} > N_{\text{theor}}$
Overlapping elements for optimum shift	$N_{\text{theor}} - N_{\text{exp}}$	N_{exp}	$N_{\text{exp}} - N_{\text{theor}}$
Probability for optimum shift and agreement of all overlapping elements	$N_{\text{exp}} / N_{\text{theor}}$	1	$N_{\text{theor}} / N_{\text{exp}}$
Zero shift ($d = 0$)	The LCR of the model is covered by the experiments; the HCR is not!	The CRs agree in experiments and theory for zero shift	Only the HCR of the model is covered by the experiments
Appearance of "empty" elements	CR not sufficient to meet with all features of the model	No empty elements if the shift is zero	Part of the results is not compatible with the model
Negative shift ($d < 0$) of theoretical vs. experimental string	The limiting case at LC is not included in the experiments		
	Same, if $N_{\text{theor}} - d > N_{\text{exp}}$	Experiments in the HCR are not considered	
Positive shift ($d > 0$)	The limiting case at HC is not covered by the experiments		Same for $N_{\text{theor}} + d < N_{\text{exp}}$

^a Abbreviations: CR, range of reactant concentrations; LCR, low concentration range; HCR, high concentration range; and LC, HC low or high concentrations respectively.

reliable, rather defined matrix [39] is based on the symbols in Sections 4.4 and 4.5, and has also been tested for some applications [40].

5.5. Calculation of the evidence factor

The information on the validity of any particular model must be related to the concept of probability. The true significance of this term is based on the selection of a "valuating" function, compressing the results of a comparison of all six strings (three experimental and three theoretical). Because this is a problem of half-order, depending on the point of view [41,42], it is good practice to speak of a (relative) evidence factor p only, which dispenses with the requirement for an absolute value. A very simple but plausible approach for comparing two strings is

$$p = \frac{B}{N_{\text{exp}} + N_{\text{theor}} - u} \quad (32)$$

where u is the number of overlapping, i.e. comparable, elements and B is the sum of ratings for the overlapping elements ($< (q - 1) N \cdot 1$, if q is the

TABLE 3

Evidence factors of the ten best two-reaction models for describing the kinetics of the reaction of triphenylphosphite, P, as reference reactant with its ozonide, PO_3^{a}

Model (TRM)	String length	Shift	Results of optimization	
			Excessive intervals at end	Evidence factor (%)
1. FAB2	7	1	0	48.7
2. P21	6	2	0	47.0
3. PAB1	6	1	-1	46.2
4. F21 *	7	0	-1	45.8
5. PAB2	5	2	-1	45.4
6. PAB	7	1	0	44.6
7. FAB1 *	5	0	-3	43.8
8. PAB *	5	2	-1	42.4
9. F2AB *	6	2	0	42.3
10. FAB2 *	7	0	-1	41.0

^a Six DTA curves: reference component $[\text{P}]_0 = 0.00, 0.026, 0.05, 0.08$ and 0.20 M; fixed component $[\text{PO}_3]_0 = 0.05$ M; solvent CH_2Cl_2 .

The following MCC was obtained and used for the rating

-) L) L + + - - 1
 2) -) H) - H) H+ - -)
 1L - - - + + M 1) (N = 8).

The simple rating matrix of Section 5.4 and eqn. (32) were used. "Empty" intervals were considered by a statistically founded hit-factor of 0.37 (algorithm $X\phi$, see Table 4).

number of reactants). For the other parameters, see Table 2. In eqn. (32), p is the relative contribution of the ratings of the comparable experimental and theoretical elements, referred to all elements of both MCCs [8].

5.6. Reaching the optimum shift

The highest p (unity) is reached if all compared elements are equal, the chains have the same length N and the MCCs have not shifted towards each other. An appearance of empty (non-corresponding) theoretical elements, i.e., mostly $N_{\text{exp}} < N_{\text{theor}}$, means that the reactant concentrations used in the experiments do not completely utilize the effective range for the signal form of the respective theoretical model, whilst the inverse case of $N_{\text{exp}} > N_{\text{theor}}$ suggests that some of the results are possibly not compatible with the theoretical model (Table 2). But it is problematical to "translate" such qualitative statements into an absolute value for the probability, and it is totally inappropriate to compare an evidence factor with a term such as the confidence level which is much higher. Nevertheless, for an experimental series this evidence factor, when fixed for the optimum shift, is capable of comparing the applicability of different models (Table 3).

6. SUPERPOSITION OF TWO TWO-REACTION MODELS

6.1. General

A two-reaction model represents a superposition of two single steps; the latter are limiting cases of it for very low or high initial concentration. The corresponding degenerate MCCs have $N = 1$ if $[A]_0 = [B]_0$. Analogously, TRMs may be understood as degenerate four-reaction models (FRMs) [7,8], and a respective combinatorial expansion of the TRM-shift program should be possible.

For the optimizing procedure there are two alternative strategies. The first, more precise one is based on two different MCCs shifted independently of each other towards a fixed experimental MCC, which, however, requires long calculation times: for 50 TRMs and, for example, eight shift possibilities, $(50 \times 8^2/2)^2 = 2.5$ million combinations that have to be evaluated. A simplified method is to start with only those shifts of the 50 source TRMs which have been shown to be the best; this procedure yields $50 \times 50/2 = 1250$ combinations only. It seems that the simple method is sufficient in most cases.

6.2. Trivial and non-trivial superpositions

The TRM set also contains the elementary reaction models 1, 2 and AB (see Section 4.2). Consequently, degenerate three-reaction models are often obtained, which are in fact TRMs only, for instance $P12 + 1 (\Rightarrow P12)$, $FAB1 + AB (\Rightarrow FAB1)$. (However, cases where the second index is repeated, i.e. $F12 + 2$, $G1AB + AB$, are non-trivial.) Another type of trivial superposition is formed by exchange of the indices of P or U types, coupled with reversing the conditions from $E1 < E2$ to $E1 > E2$, for example the couples $P21 \leftrightarrow P12^*$ or $UAB1^* \leftrightarrow U1AB$. A third type involves special combinations with competing and consecutive (“cross-over”) reactions, such as $P1T$ or $PABT$ [8,37].

All these possibilities should be eliminated before the FRM superposition is performed by the computer, because they show identical codes and do not yield any new information.

6.3. Rating, information gaps and problems of confirmation

A simultaneous overlay of two theoretical strings on the experimental string may also result in either empty or doubly occupied intervals inside the experimental string length. In the latter case, identity of all three symbols could lead to problems in rating, because a probability of unity cannot be exceeded in this interval. Then, an empirical factor can be introduced for obtaining an adequate bonus for the pay-off (see eqn. (33),

TABLE 4
Improvements obtained by using four-reaction models? (see Table 3)^a

System or theoretical file	Steps	MCC length <i>N</i>	Algorithm	Best TRM /shift/(%)	Best super-position/shifts	Percentage (gain)	Remarks
$I_2 + 0.78H_2O_2^*$	> 10	7	X ϕ	P2T*/+1 54.9 FAB2*/0 74.1	P21 + FAB2* -1, +1 G21* + PAB2 0, +2	56.3 (+1.4) 71.0 (-3.1)	Very complicated
0.05PO ₃ + P in CH ₂ Cl ₂ : [P] ₀ is varied	6-7?	8	X ϕ	FAB2/+1 48.7 F21*/0 62.4	FAB1* + P21 0, +2 F21* + 3 0, +3	52.4 (+3.7) 67.6 (+5.2)	
XPOZ2A	2	10	X ϕ	P2T/-1 41.0 F21*/+1 55.6	P2T + FAB2 -1, +2 F21* + PAB1 +1, +3	40.5 (-0.5) 55.5 (-0.1)	One autocatalytic and one unimolecular step
XPOZ4A	4	10	X ϕ	PABT/0 40.3 1B/+3 48.7	PABT + PAB1* 0, +2 F21* + 1B 0, +3	42.8 (+2.5) 56.1 (+7.4)	
XPOZ5B	5	9	X ϕ	P2T/0 46.1 P2T/0 56.7	P2T + PBA1 0, +2 P2T* + PBA1 0, +2	49.3 (+3.2) 65.3 (+8.6)	
XPOZ6	6	8	X ϕ	F21 + /0 50.1 F21 + /0 65.8	F21* + P2T* 0, +4 F21* + PBA1* 0, +3	50.3 (0.2) 69.0 (+3.2)	

^a For abbreviations of the models, see section 5.1. Some additional types occur which have been described earlier: P2T, cross-over second-order reaction $2A \rightarrow X (+A) \rightarrow \text{product(s)}$; PBA1, as PBA1 but B is the reference reactant; 1B, autocatalytic reaction $A + B \rightarrow 2B + \text{product(s)}$; 3, formal third-order reaction $3A \rightarrow \text{product(s)}$.

An asterisk means $E_2 < E_1$. X ϕ denotes the simple, X7 the refined rating matrix (Section 5.4), using eqn. (32).

below). In contrast, optimized superpositions with empty intervals inside, mean that even two strings are not capable of sufficiently reproducing the behaviour in the medium range of starting concentrations, which for the simplified strategy is considered in the individual rating formulae (eqn. (32)).

Hence a suitable expression for the FRM superposition rating p_d is [8]

$$p_d = \frac{u_1 + u_2 - 2(x_- n_g + x_+ n_d)}{u_1 + u_2} \frac{u_1 p_1 + u_2 p_2}{q_{\min}} \quad (33)$$

where p_1 and p_2 are evidence factors obtained individually from eqn. (32), u_1 and u_2 are overlapping elements of the theoretical strings, 1 and 2, with the experimental string, q_{\min} is the minimum of N_{ex} and $(u_1 + u_2)$, n_g is the number of gaps (empty elements), preventing comparisons, x_- is the loss factor because of gaps, n_d is the number of overlapping elements of the two theoretical strings and x_+ is the gain factor (bonus) because of double confirmation.

We did not find it necessary to use an x_- different from zero (see eqn. (32)). Further, the bonus factor x_+ , also used for reaching a correct validity of eqn. (33) in the case of two identical theoretical strings, was set to 0.3; the value $0 < x_+ < 0.5$ means enhancing the rating for double agreement.

The best values of x_+ and x_- are a problem in practice because all such probability concepts render arbitrary solutions [41–43]. We have determined preliminary values, based on empirical studies, utilizing as many practical examples as possible.

A simple criterion for the plausibilities of the x values is that for a true FRM the highest evidence factor reached must be higher than for the best TRM. Such a balancing adjustment can be performed using either experimental or theoretical models and their MCCs (Table 4). One conclusion derived from such evidence factor differences as observed in the columns 5 and 8 is that four-step models are truly the best for a fragmentation into two TRMs, whilst models with more or less steps are increasingly unfavourable candidates for this procedure. Extension of this approach to five-step or multistep models should be possible; the concepts for ruling the possible combinatorial variety are similar to those for efficient computer chess strategies [7,44].

7. CONCLUSION AND OUTLOOK

The expressions and procedures described are capable of evaluating thermoanalytical records performed with linearly increasing and with uniform temperatures (stirring equipment). The same procedures can be applied to theoretical files calculated for any kinetic model. For the group of two-reaction models it was found that such reference strategies (pattern

recognition in a wider sense) are very useful because now a universal set of all TRMs exists [8,39] which over the long-term development of our own software (widely expanded for testing purposes) has been proved to be adequate in every respect for a reliable non-isothermal reaction analysis [2]. A theoretical proof of the reliability can be seen in the observation that addition of a further step to a theoretical model (up to seven steps), is generally indicated by a maximal increase in the corresponding evidence factor [40]. For practical purposes, our software could be compressed considerably, possibly to 20% of the present size (see ref. 29).

The “one-step reference strategy” can also be used for interpreting isothermal plots. But such an analysis would be less effective; furthermore, the primary evaluation, based on experimental isothermal MCCs which show no S string, should then utilize a logarithmic time-scale (as is usual in many variants of normal kinetic evaluations), in order to avoid excessively long calculating times, even in the later period of second-order records.

Extensions of the concept to solid phase studies should be promising if the equipment allows a satisfactory standardization of the signal shape, in spite of temperature non-uniformity. There are basic concepts for the installation of databanks of heterogenkinetic models [35,45–47], and it is a challenging task to elaborate a universal classifying system for multistep models constructed from the various types of building blocks, which are fundamentally different from the elementary processes of the homogenkinetic types 1, 2 and AB [48].

ACKNOWLEDGEMENTS

I am grateful to the late Professor Dr. O.E. Polansky for his proposals and constant interest in this work, Professor Dr. D. Schulte-Frohlinde for further support of the studies, N. Behlau, R. Laupert, G. Mummerz, Dr. Zs. Nagy-Ungvarai, B. Pirke, B. Stilkerieg and E. Theisen for performing the DTA and UV experiments and their evaluation, the late G. Lindner for his assistance in developing the techniques, W. Angenendt, K.-H. Boll, H.-D. Schmitz and Dr. B. Weimann of the Joint Computer Department of the Max-Planck Institutes for Coal Research and Radiation Chemistry for their help in writing the computer programs.

REFERENCES

- 1 W.W. Wendlandt, *Thermochim. Acta*, 5 (1973) 225.
- 2 E. Koch, *Non-Isothermal Reaction Analysis*, Academic Press, London, 1977.
- 3 B. Wunderlich and P. Fellner, *Thermochim. Acta*, 110 (1987) 67.
- 4 R. Lutz, *Informationsentropie oder Allmaehlicher Orientierungsverlust im Datenwald*, DECFocus, Digital Equipment Corp., Munich, Germany, 57 (1989) 15.
- 5 J. Fiala, *Thermochim. Acta*, 110 (1987) 11.
- 6 J.S. Flynn, M. Brown and J. Sestak, *Thermochim. Acta*, 110 (1987) 101.

- 7 E. Koch, *Thermochim. Acta*, 121 (1987) 253.
- 8 E. Koch, *Thermochim. Acta*, 152 (1989) 387.
- 9 J.H. Flynn and L.A. Wall, *J. Res. Natl. Bur. Stand. Ser. A*, 70 (1966) 487–523.
- 10 H.J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, 79 (1957) 41.
- 11 E. Koch, *Chem. Ing. Tech.*, 37 (1965) 1004.
- 12 E. Koch, *Thermochim. Acta*, 56 (1982) 1.
- 13 E. Koch, B. Stilkerieg and L. Carlsen, *Ber. Bunsenges, Phys. Chem.*, 83 (1979) 1238.
- 14 P.C. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw–Hill, New York, 1969.
- 15 W.F. Hemminger and H.K. Cammenga, *Methoden der Thermischen Analyse*, Springer-Verlag, Berlin, 1989.
- 16 E. Koch, *J. Therm. Anal.*, 33 (1988) 177.
- 17 Ref. 2, p. 114.
- 18 H.E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
- 19 H. Anderson, *J. Therm. Anal.*, 33 (1988) 133.
- 20 H. Jüntgen and H.K. van Heek, *Fortschr. Chem. Forsch.*, 13 (1969/1970) 601.
- 21 N.N. Semenov, *Chemical Kinetics and Chain Reactions*, Oxford University Press, London, 1935.
- 22 N.N. Semenov, *Usp. Fiz. Nauk*, 23 (1940) 251.
- 23 D. Krug, *Thermochim. Acta*, 10 (1974) 217.
- 24 M. Balarin, *Phys. Lett. A*, 64 (1978) 435.
- 25 T. Ozawa, *Thermochim. Acta*, 100 (1986) 109.
- 26 E. Koch and B. Stilkerieg, *Thermochim. Acta* 17 (1976) 1.
- 27 E. Koch and B. Stilkerieg, *Thermochim. Acta*, 27 (1978) 69.
- 28 E. Koch and B. Stilkerieg, *J. Therm. Anal.*, 17 (1979) 395.
- 29 E. Koch, *J. Therm. Anal.*, 32 (1987) 259.
- 30 E. Koch, *Thermochim. Acta*, 112 (1987) 81.
- 31 E. Koch, *Thermochim. Acta*, 82 (1984) 293.
- 32 E. Koch, in: K.H. Ebert, P. Deuffhard and W. Jaeger (Eds.), *Modelling of Chemical Reaction Systems*, Springer, Berlin, 1981, pp. 216–225.
- 33 E. Koch, *Thermochim. Acta*, 110 (1987) 135.
- 34 H. Anderson, D. Haberland, and E. Witte, *Z. Chem.*, 18 (1978) 153.
- 35 E. Koch, *Angew. Chem.*, 95 (1983) 185; *Angew. Chem., Int. Ed. Engl.*, 22 (1983) 225.
- 36 J.E. House, *Thermochim. Acta*, 42 (1980) 369.
- 37 Ref. 2, Chapter 4, pp. 127–173.
- 38 E. Koch and Zs. Nagy-Ungvarai, *Ber. Bunsenges. Phys. Chem.*, 91 (1987) 1375.
- 39 E. Koch, *J. Therm. Anal.*, in press.
- 40 E. Koch, *Thermochim. Acta*, 187 (1991) 159.
- 41 R. Carnap and W. Stegmüller, *Induktive Logik und Wahrscheinlichkeit*, Springer, Vienna, 1959.
- 42 K.R. Popper, *The Logic of Scientific Discovery*, Hutchinson, London, 1965.
- 43 R.D. Luce and H. Raiffa, *Games and Decisions*, Wiley, New York, 1965.
- 44 T.A. Marsland and J. Schaeffer, *Computers, Chess, and Cognition*, Springer-Verlag, Berlin, 1990.
- 45 J.H. Sharp, G.W. Brindley and N.A. Achar, *J. Ceram. Soc.*, 47 (1966) 379.
- 46 S. Boy and K. Boehme, *Thermochim. Acta*, 20 (1977) 195.
- 47 J. Sestak and G. Berggren, *Thermochim. Acta*, 3 (1971) 1.
- 48 P.D. Garn, *J. Therm. Anal.*, 13 (1978) 581.