# APPLICATION OF COMPLEX REACTION KINETIC MODELS FOR THE LEAST SQUARES EVALUATION OF THERMOANALYTICAL EXPERIMENTS†

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## ABSTRACT

The complexity of the phenomena which arise during the heating of the various substances seldom can be described by a single reaction kinetic equation.  As a consequence, sophisticated models with several unknown parameters have to be developed.  The determination of the unknown parameters and the validation of the models requires the simultaneous evaluation of whole series of experiments.  We can accept a model and its parameters if, and only if we get a reasonable fit to several experiments carried out at different experimental conditions.  In the field of the thermal analysis the method of least squares alone seldom can select a *best* model or a *best* set of parameter values.  Nevertheless, the careful evaluation of the experiments may help in the discerning between various chemical or physical assumptions by the quality of the corresponding fit between the experimental and the simulated data.  The problem is illustrated by the thermal decomposition of cellulose under various experimental conditions.

# INTRODUCTION

The mathematical modelling of the chemical processes is a crucial problem of the thermal analysis. Without a proper model we cannot answer even a question like "Do the same reactions occur in an isothermal and a non-isothermal experiment?"  A single kinetic equation of type

$$k = A \exp(-E/RT) \, f(\alpha) \tag{1}$$

can seldom describe the real complexity of the phenomena arising during the heating of the various substances.  However, if we are able to eliminate experimentally the effect of the transport processes, it is possible that a system of ordinary differential equations can be applied.  Even in that case we shall have much more than three unknown parameters.  The determination of the unknown parameters and the validation of the model requires the simultaneous evaluation of a whole series of experiments.  We can accept a model and its parameters if, and only if we get a reasonable fit to a whole series of experiments with different experimental conditions.

In this paper general questions and special problems of the evaluation will be discussed.  As an illustration, examples will be presented from our former work dealing with the thermal decomposition of cellulose at various experimental conditions [1–4].

# NOTES ON THE METHOD OF LEAST SQUARES

The most straightforward way to obtain a reasonable fit for a series of experimental curves is the application of the method of least squares.  Denoting the experimental data (sample mass, DSC signal, etc.) by $X^{obs}$ and the corresponding points of the calculated functions by $X^{calc}$, respectively, we search for those values of the unknown parameters at which the sum

$$S = \sum_{j=1}^{M} \sum_{i=1}^{N_j} [X^{calc}(i,j) - X^{obs}(i,j)]^2 / N_j M \tag{2}$$

is minimal.  Here $M$ is the number of experimental curves used in the evaluations and $N_j$ is the number of points on the $j$th experimental curve.  The resulting fit can be expressed as

$$fit \, (\%) = 100 \, S^{1/2} / X_{highest} \tag{3}$$

Here $X_{highest}$ is the highest observed value, for example the initial sample mass or the highest amplitude on a DSC curve.
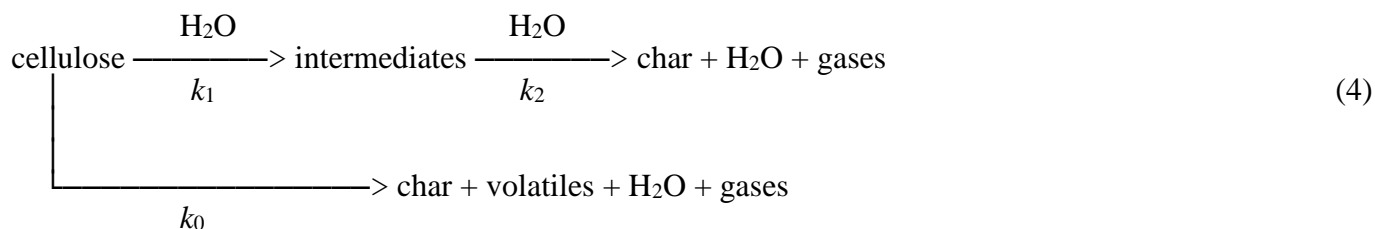
We should like to underline that the method of the least squares is not a consequence of any elegant mathematical principle in the case of thermal analytical measurements. The problem is that the errors of the individual experimental points, $X^{calc}(i,j)$ are neither random nor independent of each other. In modern thermal analysis, the random components of the errors are filtered out almost completely by the hardware of the apparatus and by the computerized data acquisition. The main components of the experimental errors are systematic and may vary from experiment to experiment. In this way we cannot employ the usual deduction of the method of least squares from the principle of the maximum likelihood.

As a consequence, we cannot say that the obtained parameters are the *best.* We can judge only the curve fitting capabilities of a given model with a given set of parameters. Nevertheless, if the model describes the observations in a wide range of experimental conditions *and* the obtained parameters are in accordance with other sources of knowledge *then* we can hope that the approximation is not formal.

Finally a few notes about the quantities X for which the method of least squares can be employed. We firmly disapprove the use of any arbitrary transformations of the observations. The use of the logarithm of the observations, for example, strongly decreases the capabilities of the method. The high speed and low price of the desktop computers of our age exclude any needs for the classical linearization techniques. The only reason that can justify a mathematical transformation is if it helps to discern better between the various models or parameters. A well-known example is the least squares evaluation of the DTG curves in case of models which differ from each other mainly by the shape (asymmetry) of the reaction rate curves. In that case, however, care should be taken to ensure that the numerical differentiation of the sample mass curve do not lead to distortion or loss of information.
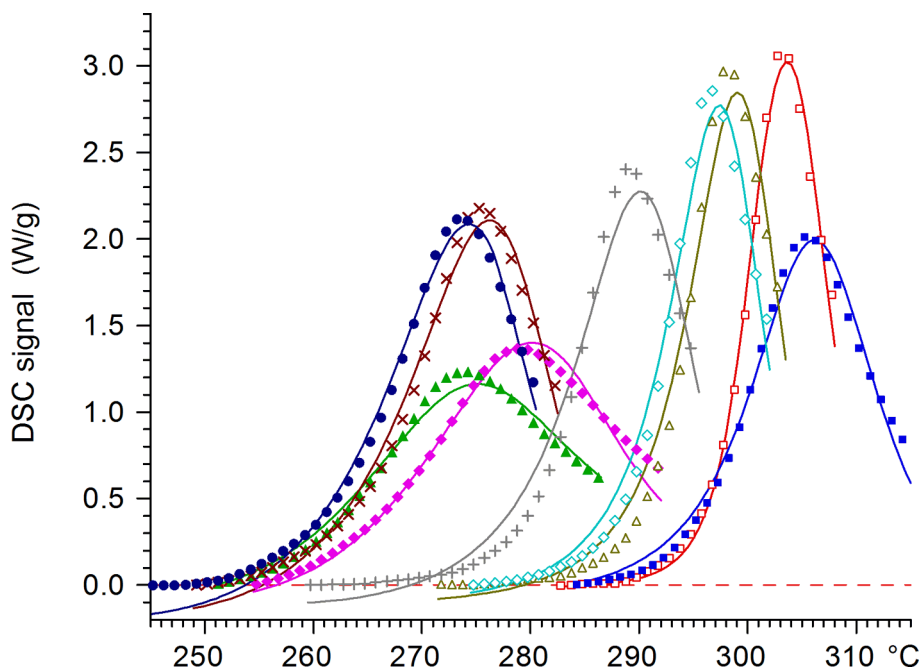

## KINETICS OF THE THERMAL DECOMPOSITION OF CELLULOSE IN SEALED VESSELS AT ELEVATED PRESSURES [1]

We studied the thermal decomposition of pure cellulose in sealed sample holders by a computerized Setaram DSC 111 differential scanning calorimeter. To ensure chemical kinetic control of the decomposition, the heat transfer problems were reduced by applying low heating rate (5°C/min) and relatively low amounts of cellulose (5 - 10 mg). The pressure during the decomposition was estimated in separate experiments and was found to be between 3 and 15 MPa. Some of the experiments were carried out with the addition of 0.6 to 1.8 mg water to the cellulose. Under these experimental conditions we proved the validity of the following reaction kinetic scheme

$$\text{cellulose} \xrightarrow[\; k_1 \;]{\; H_2O \;} \text{intermediates} \xrightarrow[\; k_2 \;]{\; H_2O \;} \text{char} + H_2O + \text{gases}$$

$$\xrightarrow[\; k_0 \;]{} \text{char} + \text{volatiles} + H_2O + \text{gases} \tag{4}$$

Here $k_0$, $k_1$ and $k_2$ are rate constants for reactions 0, 1, and 2, respectively.  Reaction 0 is the non-catalyzed decomposition observed in open pan TG experiments.  Reaction 1 is the solid state reaction of cellulose in the presence of water.  Reaction 2 is the secondary reaction of the intermediates in the sealed sample holder. Reactions 1 and 2 are catalyzed by the water arising from three sources: (i) initial moisture content of the samples; (ii) extra water added optionally before the start of the experiments; (iii) water formed as a major decomposition product.

The corresponding mathematical model consisted of a system of  four ordinary differential equations which contained eight unknown parameters.  The determination of the unknown parameters required the simultaneous evaluation of nine experiments.  (See Figure 1.)  The experiments shown in Figure 1 differed in the water vapour concentration of the gas phase due to the different sample mass and/or to the addition of extra water before the start of the reactions.  When a higher amount of cellulose was enclosed in the sample holder, more water produced and the acceleration of the reaction occurred at lower temperature.  A similar effect was obtained by adding an extra amount of water to the samples.



**Figure 1.**  Thermal decomposition of cellulose in hermetically sealed sample holders [1].  Nine high pressure DSC experiments are shown, differing from each other by the sample mass and/or the amount of water placed into the sealed sample holders. The experiments are represented by different symbols (●, x, ▲, ◆, +, ◇, △, □, ■ ). The solid lines stand for the simulated curves which were obtained by a simultaneous least squares evaluation based on reaction scheme (4).

It turned out during the evaluation that the experiments could not be described by *exactly* the same set of kinetic parameters.  As an explanation we assumed that the systematic errors of the high pressure DSC experiments slightly distorted the experimental curves and this distortion differed from experiments to experiments.  However, the model proved to be applicable when a small scattering was allowed for each parameter.  Allowing the parameters to have slightly different values in the different experiments is a simple technique to describe formally the effect of the systematic errors.  Obviously we can not say in that case that a certain set of parameter is the *best*.  However, we are still able to observe whether a chemical assumption improves or spoils the fit between the observed and the calculated data.  As an example we may note that reaction scheme (4) gave much better fits when we allowed the water yield of reaction 1 to be negative.  In this way the model clearly indicated that reaction 1 consumes water, which means that the upper reaction route in scheme (4) starts with a hydrolysis.
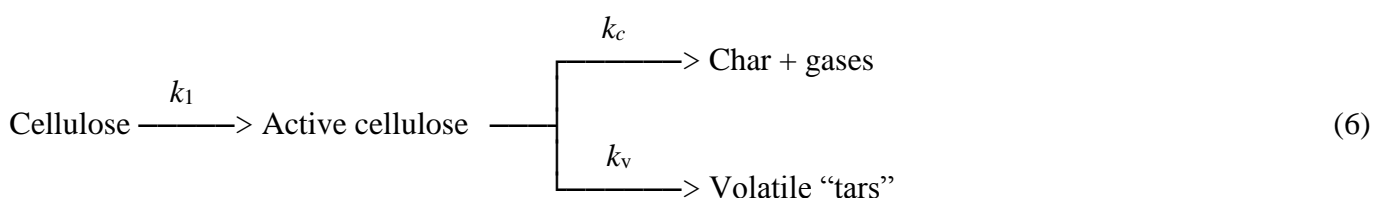
## KINETICS OF THE THERMAL DECOMPOSITION OF CELLULOSE IN OPEN SAMPLE PANS AT LOW AND MODERATE TEMPERATURES [2]

Broido and his coworkers have shown that cellulose decomposes by a multistep mechanism at low temperatures.  Their established the following reaction scheme for the temperature domain $220 - 270°C$ [5]:

$$\text{"A"} \xrightarrow{k_b} \text{"B"} \begin{cases} \xrightarrow{k_c} \text{"C"+...} \xrightarrow{k_d} \text{"D"+...} \xrightarrow{k_e} \text{"E"+...} \\ \xrightarrow{k_v} \text{volatile "tars"} \end{cases} \tag{5}$$
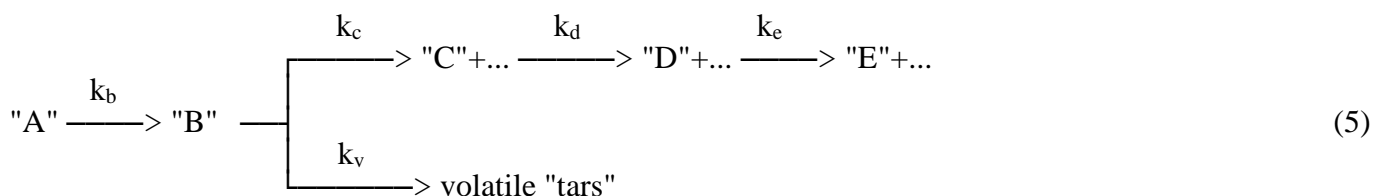
where "A" denotes the unreacted cellulose which quickly transforms to a so called "active cellulose", "B" with rate constant $k_b$. The active cellulose decomposes further by two competitive mechanisms. "C", "D" and "E" represent solid intermediates in a sequence of consecutive reactions. The ellipses with the plus sign, "+ ..." indicate volatile formation.

Later Bradbury, Sakai and Shafizadeh [6] simplified Broido's reaction network by omitting the reactions leading to *"D"* and *"E"* in the upper branch:

$$\text{Cellulose} \xrightarrow{k_1} \text{Active cellulose} \begin{cases} \xrightarrow{k_c} \text{Char + gases} \\ \xrightarrow{k_v} \text{Volatile "tars"} \end{cases} \tag{6}$$

This simplified reaction scheme, called the "*Broido-Shafizadeh model"*, is generally accepted today and the kinetic parameters presented by Bradbury et al. [6] are frequently quoted and used in simulations. Nevertheless, schemes (5 – 6) can be criticized as an over-simplification of extremely complex chemical and physical phenomena.  One rationale for the modelling of complicated organic reactions by simplified reaction schemes is that a partial reaction in the scheme  may correspond in reality to a group of reactions. For example, a partial reaction may be the average of several parallel reactions or the slowest step in a sequence of consecutive reactions.
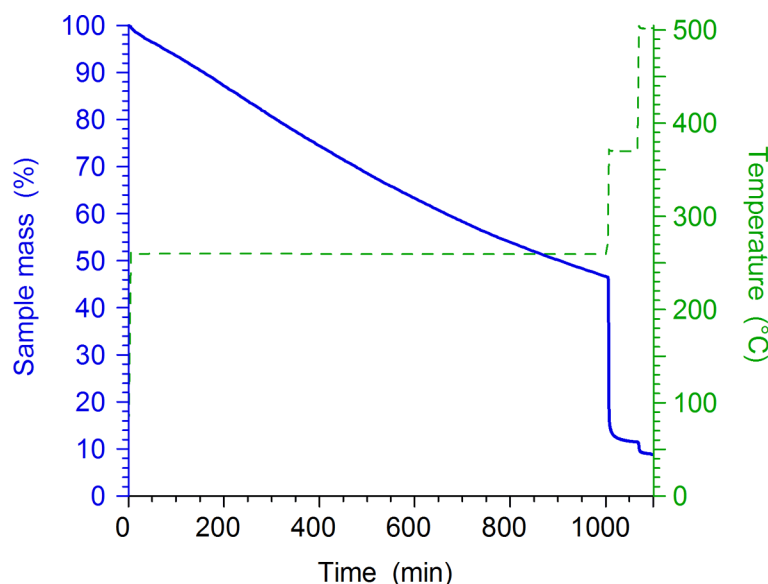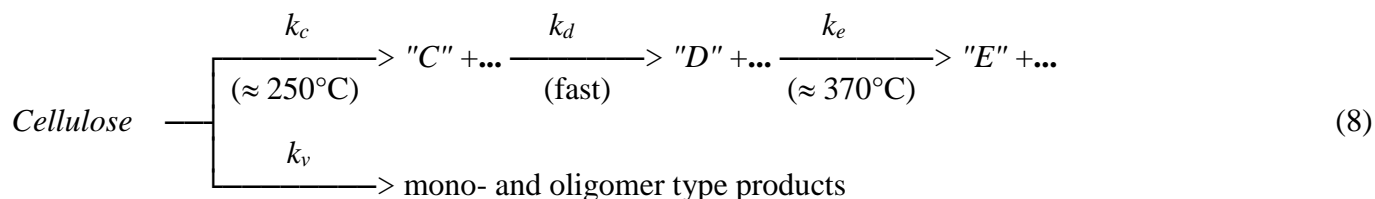


**Figure 2**.  Thermal decomposition of cellulose in open sample pans.  A typical thermogravimetric experiment is shown which were used by the authors to check the validity of reaction schemes (5), (6) and (8).  Here the bold solid and thinner dashed lines represent the experimental sample mass and temperature curves, respectively.

As the temperature increases, the lower branch of reaction schemes (5 – 6) becomes dominant and the overall reaction can be described by a single first order reaction.  To investigate the whole reaction scheme we carried out experiments with temperature programs containing isothermal sections of 30 – 999 minutes connected by temperature ramps of 40°C/min.  A typical experiment of this type is shown in Figure 2.  In the time of the earlier workers of the field [5–6] only a single isothermal section of a thermoanalytical curve could be used in the evaluation.  However, the high level computing facilities of our age permits the simultaneous evaluation of a group of experiments by solving the system of kinetic differential equations along the given temperature vs. time functions.  When we carried out a simultaneous least squares evaluation of five experiments with different temperature programs, it turned out that fit is better if the

cellulose —> active cellulose                                                                                          (7)

reaction is omitted from reaction schemes (5-6).  Note that this reaction does not result in mass loss hence there had not been any direct proof of its existence in the temperature domain of the thermal decomposition.

Our results indicated that reaction (7) either completes *before* the start of the mass loss or does not take place at all.  Extending the study to 370°C, we obtained the following reaction scheme:

$$
Cellulose \begin{cases} \xrightarrow[\substack{(\approx 250°C)}]{k_c} \text{"C"} + \text{...} \xrightarrow[\text{(fast)}]{k_d} \text{"D"} + \text{...} \xrightarrow[\substack{(\approx 370°C)}]{k_e} \text{"E"} + \text{...} \\ \\ \xrightarrow{k_v} \text{mono- and oligomer type products} \end{cases}
\tag{8}
$$

where *"C", "D"* and *"E"* are solid intermediate products and the ellipses (...) indicate volatile formation.  The corresponding fit between the experimental and the calculated curves are shown in Figures 3/a and 3/b, which exhibit the lower and the upper temperature domains of the five experiments evaluated simultaneously.
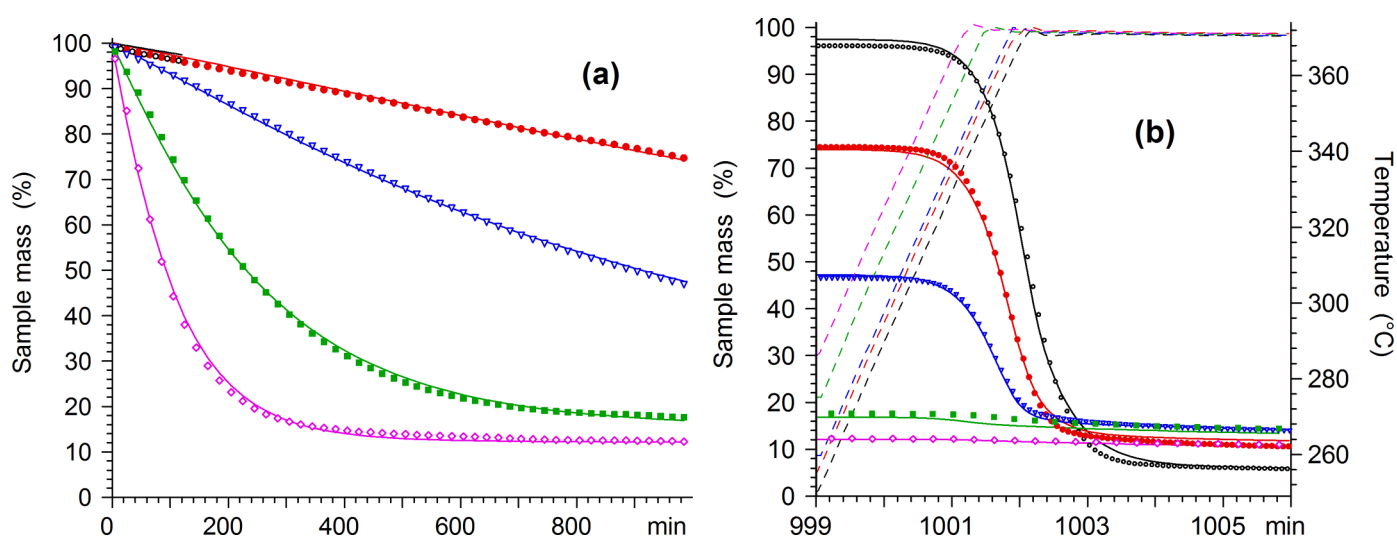


**Figures 3/a – 3/b**.  Simultaneous least squares evaluation of five cellulose TG curves during a long isothermal section **(a)**, and during the subsequent heating to a second, high temperature isothermal section **(b)**, respectively [2].  The evaluation was based on reaction scheme (8).  The symbols (○ ● ∇ ■ ◇) and the solid lines represent the observations and the simulated curves, respectively.  The following low temperature isothermal sections were employed:  120 min at 250°C (○), 999 min at 250°C (●),  999 min at 260°C (∇),  999 min at 275°C (■) and 999 min at 286°C (◇), respectively.  In Figure 3/b the dashed lines represent the temperature.  Here the time scale of the experiment with 120 min preheating (○) starts at 120 min.

## CONCLUSIONS

1)  The complexity of the phenomena which arise during the heating of the various substances requires the development of sophisticated models with several unknown parameters.

2)  The modern computing facilities permit the simultaneous least squares evaluation of a group of experiments by solving the system of kinetic differential equations along any T(t) temperature programs.

**3)** In the field of the thermal analysis the method of least squares alone seldom can select a *best* model or a *best* set of parameter values.  Nevertheless, the careful evaluation of a whole series of experiments may help in the discerning between various chemical or physical assumptions by the quality of the corresponding fit between the experimental and the simulated data.

## ACKNOWLEDGMENTS

## REFERENCES

**1.** G.Várhegyi,  P.Szabó,  W.S.L.Mok,  M.J.Antal, Jr.:
Kinetics of the thermal decomposition of cellulose in sealed vessels at elevated pressures. Effects of the presence of water on the reaction mechanism.
*J. Anal. Appl. Pyrol.*, **26** (1993) 159-174.

**2.** G.Várhegyi,  E.Jakab,  M.J.Antal, Jr.:
Is the Broido - Shafizadeh model for cellulose pyrolysis true?
*Energy Fuels*, **8** (1994) 1345-1352.

**3.** G.Várhegyi,  P.Szabó, M.J.Antal, Jr.:
Kinetics of the thermal decomposition of cellulose under the experimental conditions of thermal analysis. Theoretical extrapolations to high heating rates.
*Biomass Bioenergy*, **7** (1994) 69-74.

**4.** M.J.Antal, Jr.,  G.Várhegyi:
Cellulose pyrolysis kinetics: The current state of knowledge.
*Ind. Eng. Chem. Res.*, **34** (1995) 703 – 717.

**5.** A. Broido,  M. Weinstein:
Kinetics of Solid-Phase Cellulose Pyrolysis.
In *Proc. 3rd Internat. Conf. Thermal Anal.*, Wiedemann, Ed., Birkhauser Verlag, Basel, **1971**, pp.285-296.

**6.** A.G.W. Bradbury,  Y. Sakai,  F. Shafizadeh
 A Kinetic Model for Pyrolysis of Cellulose
*J.Appl. Polym.Sci.* **23** (1979), 3271-3280.