Journal of Thermal Analysis, Vol. 35 (1989) 547-553

APPLICATION OF ARTIFICIAL INTELLIGENCE FOR THE DETERMINATION OF REACTION MECHANISMS

E. Koch

MAX-PLANCK-INSTITUT FÜR STRAHLENCHEMIE
D-4330 MÜLHEIM A. D. RUHR

ABSTRACT. TA curves can be interpreted kinetically by pattern recognition. Readily available symbol strings are compared with those of theoretical curves, stored in a data bank. Such kinetic codes fix the dependences of the mechanistic coordinates on the initial concentration of **one** of the reactants; obviously, they are scarcely influenced by the prevailing values of the activation parameters.

The foundations for a model-determinating computer program and the experiences with its application are presented. The program reveals the possible homogeneous two-reaction models from an experimental DTA- or non-isothermal UV-series; these are listed in the order of their evidence values. Similarly, the best superpositions of two two-reaction models are determined.

INTRODUCTION

The aim of kinetic studies is the determination of the reaction mechanism responsible for the temporal behavior of a given reacting system. Kinetic values are meaningless if the mechanism is unknown; this theme was intensively discussed during the ICTA 8th in Bratislava and ESTAC 4 in Jena [1].

However, measurements performed at homogeneous conditions allow a relatively simple interpretation when obtained by the use of thermoanalytical equipment since the time-linear increase of temperature enables one to recognize the elementary partial steps more selectively [2]. This could be recently confirmed for the example of the very sophisticated oscillating Belousov-Zhabotinsky reaction [3]. Powerful new capabilities are offered by generating theoretical signal curves based on assumed models, using effective integration algorithms. Being concerned with such simulations for various model types for a long period, an operator must have the feeling that every model has his own, specific features. It may even be supposed that these are mainly independent of the activation parameters, and, probably, of the signal parameters.

Does such a THEOREM OF COMMON KINETIC RUNS really exist? There is no exact mathematical proof up to now; but our knowledge about elementary processes, as was presented in a "THEORY OF THE CHARACTERISTIC RATE COEFFICIENTS" recently [4], must raise the expectation that the well-reasoned application of computers may lead to a semi-empirical proof in the next years. This optimism is strengthened by the structure of the semi-empiric expressions for the standardization of halfwidth and shape index of DTA curves [5,6] which implicitly make use of the basic signification of the ***ratio activation energy over square of the logarithmic A-factor*** in elementary non-isothermal kinetics, discovered already 1930 by N.N.Semenov [1,6]. Based on the corresponding ***invariance*** character of the ***mechanistic coordinates*** and on the principles of pattern recognition and mental concentration, which is essential for any extension of knowledge [7], we have developed a computer program which transforms a ***code string***, obtained from an series of experiments, into a list of all possible two-reaction models, ordered with respect to their ***evidence values***. An additional algorithm allows also the interpretation of reactions with three or four steps if the kinetics is determined by two different models, one valid at low, the other at high reactant starting concentrations.

The problems arising during the elaboration of such a program show surprising analogies to the problems with chess programs because they are also based on combinatorical aspects and on artificial intelligence [8]. In a chess program, valuation numbers are needed which quantify all positions up to a scheduled search depth, in order to make a decision. For a kinetic scheme, corresponding various possibilities exist to append a further reaction step. Valuation numbers can be defined similarly, and the match of two opponents in a game is replaced by the comparison of an experimental with a theoretical scheme. Consequently, programs for the model determination must be based on similar strategies as chess programs; for both, the laws of game and decision theory are valid [9].

The prerequisites needed for the development of an efficient program for mass-action kinetics were:

1. An apparatus for homogeneous conditions ("all-liquid"-system)
2. A satisfactory theory for the kinetic evaluation of conversion-referred measuring curves and DTA curves
3. Adequate integration programs (e.g. of the Gear type)
4. Creation of theoretical data sets of rate curves for varied starting concentrations, involving all one- and two-step models
5. Elaboration of algorithms both for the determination of the activation data (by utilizing the dependence of the rate constant on temperature) and of the ***mechanistic concentration codes (=MCC's)***, available from the concentration dependence of the mechanistic coordinates (cf. 4.)

COMPARING EXPERIMENTAL WITH THEORETICAL STRINGS

A ***MCC*** consists of three ***strings*** of the same length which fix the type of dependences of the S-index, M(init.)- and M(overall)-index on the ***initial concentration*** of one reactant, using the symbols "+", "-" and "C" (constant). The symbol "C" may be differentiated into L(ow) < 1 < M(edium) < 2 < H(igh), indicating the formal order of reaction directly.

MCC's obtained experimentally were compared element per element with 32X3 theoretical strings of the possible two-step models, stored in the data bank. Different valuating algorithms were tested. In the simplest case, for equality of two elements the valuating number is 1, for inequality zero. However, different scales may be used between these limit cases. Then, the numbers were summarized over all string elements of the three coordinates and referred to one coordinate (=valuating sum B).

In the optimization procedure, ***shifts*** between the strings may occur, because in general the activation parameters are different for experiments and simulations, so that the total ranges of the initial concentrations are also different. In addition, the ***lengths*** (=numbers of elements) of both strings may not be identical. Despite this, plausible ***evidence values (probabilities?)*** can be calculated for a given model by referring the valuating sums to one concentration interval, using the following equation:

$$p = \frac{B}{q_{ex} + e_{th}} = \frac{B}{q_{ex} + q_{th} - u} \qquad (1)$$

q_{ex} = number of elements in the experimental string
q_{th} = number of elements in the theoretical string
e_{th} = number of empty spaces in the theoretical string
u = number of overlapping intervals

Other formulations were also tested, but proven to be less adequate.

Another expression is obtained if there is surely no alternative to a two-step model. In this case, the empty intervals of the theoretical strings can be occupied by the first and last theoretical elements, since in such ultimate intervals a constant limit behaviour has been reached.

RESULTS

Studies of 100 systems in most cases confirm the special reaction mechanisms proposed in the literature or elaborated in our laboratory (for further details, see [10]). In the synopsis of the ***evidence values*** and other significant quantities towards the number of experiments per series, which corresponds to a monotonously increasing number of participating reactions (=complexity), it becomes obvious that the best adaptions do not surpass 64% (two steps) or 70% (three our four steps). The ***average evidence values*** are only 45% or 50%, respectively. Hence, the superposition algorithm leads to better approximations; this had been expected. However, for the description of the greatest part of the reactions studied even four steps are not sufficient. Consequently, such listed two-step models must represent subsystems of a rather complicated mechanism.

SUMMARY AND OUTLOOK

What is the reason that evidence values of ca. 70% were never surpassed? Such values are rather low when compared with quantities such as correlation coefficients, confidence levels etc.. But it has to be considered that an approach to ***100% probability (=certainty)*** can never be reached for this type of quantity since such a demand would require equal lengths of theoretical and experimental strings, identity of all elements, and absence of any experimental error and any inaccuracies in the computer calculations. Generally, the conditions for experiments and simulations cannot agree in all details. Consequently, the percentages calculated by equ.(1) should rather be seen as relative probabilities, ***evidence values;*** in any case they should allow to indicate the best models in a list.

The program may also be applied to isothermal codes, then revealing less selectivity (cf. [11], tables in the appendix). After the creation of further model libraries, series based on other transmitter parameters (heating rate, packing density, sample mass etc.) as well as heterogeneous series could be subjected to a systematic kinetic investigation.

The main problems on this way are: Absence of a fully satisfactory principle for classification of heterogeneous models, difficulties in formulating absolute probabilities, lack of a general proof of the THEOREM OF COMMON KINETIC RUNS (which would restrict the numbers of simulations needed by orders of magnitude), and the indispensible improvement of the technique, especially the development of correction procedures in order to use also commercial equipment for the determination of standardized activation data, halftimes and shape indices.

REFERENCES

1 J.S. Flynn, M. Brown and J. Sestak, Thermochim. Acta 110 (1987) 101.

2 E. Koch, Non-isothermal Reaction Analysis, Monograph, 1977, Academic Press, London.

3 E. Koch and Zs. Nagy-Ungvàrai, Ber. Bunsenges. Phys. Chem. 91 (1987) 1375.

4 E. Koch, J. thermal Anal. 32 (1987) 259.

5 E. Koch and B. Stilkerieg, Thermochim. Acta 17 (1976) 1.

6 E. Koch, Thermochim. Acta 82 (1984) 293.

7 D.G. Hofstadter, Goedel, Escher, Bach, German Edition, Klett, Stuttgart, 1979.

8 E. Koch, Thermochim. Acta 121 (1987) 253.

9 R.D. Luce and H. Raiffa, Games and Decisions, Wiley, New York, 1965.

10 E. Koch, Thermochim. Acta, in preparation.

11 R. Schmid and V.N. Sapunov, Non-formal Kinetics in Search for Chemical Reaction Pathways, Verlag Chemie, Weinheim, 1982.

Zusammenfassung

Ein kinetisches Auswerteverfahren wird beschrieben, das für jedes homogene System, welches einer thermoanalytischen Messung bei konstanter Heizrate unterworfen werden kann, eine Liste der wahrscheinlichsten Ein- bis Vierstufenmodelle ausgibt. Aus der Konzentrationsabhängigkeit der mechanistischen Koordinaten (korrigierter Formfaktor und Reaktionstypindex) werden charakteristische Zeichenketten erhalten und in einem Mustererkennungsverfahren mit den analog berechneten Zeichenketten aus den Konzentrationssätzen aller denkbaren Modelle verglichen.

Резюме - Кривые ТА могут быть интерпретированы кинетически путем опознавания модели. Легко доступные символы колон сопоставлены с таковыми для теоретических кривых, помещенных в банке данных. Такие кинетические коды устанавливают зависимости механистических координат от начальной концентрации одного из реагентов. Очевидно, что они едва ли затрагиваются преобладающими величинами активационных параметров. Представлены основы для модель-определяющей компьютерной программы и опыты по ее применению. Исходя из экспериментальных данных ДТА или неизотермических УФ-серий, программа показывает возможные гомогенные двухреакционные модели, перечень которых приведен в порядке их очевидности. Подобно было определено наилучшее совпадение двух типов двух реакционных моделей.