Thermochimica Acta, 229 (1993) 321–322
Elsevier Science Publishers B.V., Amsterdam

Note

Approximative methods for the interpretation of thermokinetic measuring curves with a view to "fuzzy technology" [1]

Erhard Koch

Max-Planck-Institut für Strahlenchemie, 35470 Mülheim a.d. Ruhr (Germany)

(Received and accepted 24 May 1993)

Abstract

The argument is put for the application of fuzzy set theory to thermokinetic measuring curves.

The interpretation of "thermokinetic" measuring curves which, when applied to the effects of thermal delay and thermal feedback, reveal the momentary reaction rate derived from the deviations of the sample temperature from linearity, actually leads to requirements which cannot be met by the classical "two-values" logic that has been sufficient for the last 2000 years.

Suitable means for solving the problem of determining the prevailing kinetic model are semi-empirical mathematical expressions and iterative approximation procedures (which are run on the computer in a way similar to the controlling processes), i.e. manipulations of unsharp sets using unsharp algorithms.

Such tools are characteristics of the fuzzy set theory [1], founded mathematically by Zadeh in 1965, which is based on labels of fuzzy sets (the key elements of human thinking) and heuristic parameter correlations with rational efficiency values ("grades of membership" according to Zadeh) of between 0 and 1 ("false" and "true") which are similar to the evidence factors used in our recent rating studies.

This theory, which was first successfully applied to technological problems in Japan, is often successful in the solution of practical problems where an approach is hampered by very complex mathematics. The application of this kind of approach to thermal analysis has been demonstrated in five typical problems, with promising results.

1. The development of "mechanistic" master curves in heterogeneous kinetics [2].

[1] Presented at the Tenth Ulm Conference, Ulm, Germany, 17–19 March 1993.

2. The calculation of the reaction-specific (reduced) time u as a pre-step in the study of complex models in homogeneous kinetics [3].

3. The application of approximative expressions, developed by computer simulations, for the correction of the mechanistic coordinates S and M. For the determination of the model, this removes the deconvolution of individual TA curves and leads to a plausible, satisfactorily applicable theory [4].

4. Selection and fit of an adequate type of baseline [4, 5].

5. The precalculation and optimization of initial and final times for the numerical integration of the system of differential equations to be taken for the selected model [6].

The last operation is very important for interrelations between theory and practice, because if a complex model is assumed to be valid for a series of experiments, it can only be satisfactorily confirmed by accompanying numerical integration. In the case of an inappropriately chosen time or temperature interval, consequent distortions of frequently appearing extreme or exotic, e.g. negative, concentrations may occur, expecially in rigid systems [7]. Hence, a satisfactory model determination needs a package of communicative computer programs bearing characteristics of expert systems, and starting with our one-step reference strategy which, after a failure, is expanded iteratively by adding an additional reaction step. Studies in this Institute have confirmed that such a procedure can be controlled by continuous comparison of the experimental results with the theoretical foundations, which have both been reduced to the form of mechanistic codes of the model momentarily selected. The subsequent decisions occur by evaluation tests. Therefore, automatically controlled integrations based on systematic sets of models will be an obligatory means for this type of pattern recognition [4].

REFERENCES

1 L.A. Zadeh, Inf. Control, 8 (1965) 338.
T. Tilly, Fuzzy Logik, Franzis, Munich, 1991.
2 J.M. Criado, Thermochim. Acta, 24 (1978) 186.
J. Sestak and G. Berggren, Thermochim. Acta, 3 (1971) 1.
E. Koch, Angew. Chem. Int. Ed. Engl., 22 (1983) 225.
3 N.N. Semenov, Usp. Fiz. Nauk, 23 (1940) 251.
E. Koch, Thermochim. Acta, 56 (1982) 1.
4 E. Koch and B. Stilkerieg, Thermochim. Acta, 17 (1976) 1; 27 (1978).
E. Koch, Thermochim. Acta, 203 (1992) 43.
5 W.F. Hemminger and S.M. Sarge, J. Therm. Anal., 37 (1991) 1455.
G. Xaing and L. Yuliang, Thermochim. Acta, 150 (1989) 53.
6 E. Koch, J. Therm. Anal., 32 (1987) 259.
7 D.D. Warner, J. Phys. Chem., 81 (1977) 2329.
D. Edelson, J. Chem. Educ., 52 (1975) 642.