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THE THEORY AND PRACTICE OF THERMOANALYTICAL KINETICS OF SOLID-STATE REACTIONS

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Workshops on kinetics have become a feature of ICTAC Congresses and are generally well-attended and result in lots of useful discussion. The Workshop at ICTAC 13 continued the tradition with about 50 attendees. The workshop was chaired by Haruhiko Tanaka and Michael Brown. Six introductory presentations were made on the subject, followed by the discussion summarized below. The six introductory speakers were: (1) Ranjit K. Verma; (2) Mike Reading; (3) Crisan Popescu; (4) Erwin Kaiserberger; (5) Mike Brown; (6) Haruhiko Tanaka.

(1) The popularity of thermoanalytical kinetics of thermal decomposition of inorganic compounds with special reference to dehydrations

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The versatility of different thermoanalytical techniques has overwhelmed inorganic chemists and there has been a recent trend of using thermal analysis for a variety of inorganic studies. Kinetics is the most popular among such studies. For example, varieties of hydrated and anhydrous metal salts of hydroxy acids (e.g. lactic acid [1, 2]) and those of even simple carboxylic acids [3, 4] involving different metals and sometimes involving a series of carboxylic acids have recently been studied using thermogravimetric analysis and the data thus obtained under different specified conditions have been subjected to kinetic and mechanistic analyses. Some carboxylates have also been used frequently to test the efficacy of a new method. Although, the kinetic parameters approximated, are many times used to understand the thermal lability etc. of a group in a more meaningful way [1, 5, 6] and sometimes the procedural variables do not affect the results [7], the procedures adopted are sometimes not beyond question. The question on efficacy of non-isothermal methods on grounds of the dependency of the values of the kinetic parameters on local factors or the procedural factors does not affect the popularity of those methods.

References

1 R. K. Verma, L. Verma and M. Chandra, Ind. J. Chem., 42 (2003) 2982.
2 R. K. Verma, L. Verma, M. Chandra and B. P. Verma, J. Indian Chem. Soc., 75 (1998) 162.
3 Y. Masuda, K. Hirata and Y. Ito, Thermochim. Acta, 203 (1992) 289.
4 Y. Masuda and Y. Ito, J. Thermal Anal., 38 (1992) 1793.
5 B. A. A. Balboul, A. M. El-Roudi, E. Samir and A. G. Othman, Thermochim. Acta, 387 (2002) 109.
6 S. B. Kanungo, J. Indian Chem. Soc., 81 (2004) 644.
7 M. Samtani, D. Dollimore and K. S. Alexander, Thermochim. Acta, 392 (2002) 135.

(2) Kinetics in thermal methods, Back to the future

M. Reading, University of East Anglia, UK

Kinetics has been a controversial subject for many years. It was the focus of this workers research interests in the late 1970s with an occasional revival since [1–5]. An extensive review [6] from around that period commented that ‘the kinetic parameters most frequently used to provide information about the (reaction) step identified as rate limiting are A and E_a. Values for nominally the same chemical change often show significant deviations’. It seems that, 24 years later, matters have not significantly improved. The central question was and remains what methods are likely to give the correct answers. Unless this question is addressed there can be no progress on the debate about whether it is possible to measure ‘meaningful’ kinetic parameters in the normal use of this term. It is this question that will be briefly discussed.

References

1 M. Reading, D. Dollimore, J. Rouquerol and F. Rouquerol, J. Thermal Anal., 29 (1984) 775.
2 M. Reading, Thermochim. Acta, 135 (1988) 37.

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1388–6150/$20.00

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Springer, Dordrecht, The Netherlands

3 M. Reading, D. Dollimore and R. Whitehead, J. Thermal Anal., 37 (1991) 2165.
4 D. Dollimore and M. Reading, Application of Thermal Analysis to Kinetic Evaluation of Thermal Decomposition, Treatise on Analytical Chemistry, Part 1, Vol. 3. (Ed. J. D. Winefordner) Wiley, 1993.
5 M. Reading, Constant Rate Thermal Analysis and Related Techniques, Handbook of Thermal Analysis, Vol. 1, (Ed. M. E. Brown) Elsevier, Amsterdam 1998.
6 M. E. Brown, D. Dollimore and A. K. Galwey, Reactions in the solid-state, Vol. 22 of Comprehensive Chemical Kinetics (Eds C. H. Bamford and C. F. H. Tipper) Elsevier, Amsterdam 1980.

(3) Non-isothermal kinetics and prediction of the life-time of materials: is there any limit?

C. Popescu, DWI, Germany

The scope of a kinetic investigation is to calculate the kinetic parameters and the kinetic model for the studied process. The results are further used for predicting the behaviour of the system under various circumstances. This holds for both isothermal and non-isothermal kinetic investigations, and it is accepted as axiomatic that the kinetic results of the two types of investigations are the same [1].

Using several examples of processes occurring within various systems (explosives [2], polymers [3, 4], biological materials [5]) I question: *i*) whether isothermal and non-isothermal analyses lead always to equivalent results, and *ii*) the limits of our power of predicting the behaviour of a system from non-isothermal analysis data only.

References

1 C. Popescu and E. Segal, Int. J. Chem. Kin., 30 (1998) 313.
2 W. P. C. de Klerk, C. Popescu and A. E. D. M. van der Heijden, J. Therm. Anal. Cal., 72 (2003) 955.
3 St. Bräse, St. Dahmen, C. Popescu, M. Schroen and F.-J. Wortmann, Polym. Degrad. Stab., 75 (2002) 329.
4 P. Budrugeac, Polym. Degrad. Stab., 74 (2001) 125.
5 P. Adonyi, poster, ICTA-7, Bratislava 1984.

(4) Introducing Netzsch thermokinetics – a software module for the kinetic analysis of thermal measurements using multivariate non-linear regression

E. Kaisersberger, E. Moukhina and J. Opfermann, Netzsch

The Netzsch Thermokinetics program is applied to multiple (up to 16) isothermal and/or dynamic (heating) measurements. Through this multiple-curve analysis (multivariate analysis), with which several measurements run at different heating rates and/or isothermal measurements run at different temperatures are combined in one analysis, the behavior of the sample is examined in a global range of the reaction field [1]. With the greater amount of information now available as compared to a single curve, the desired improvement for distinguishing reaction types is achieved.

The kinetic evaluation starts with application of model free, isoconversional methods to achieve starting parameters for the further analysis and to get information about the change of activation energy with the progress of a reaction.

With multivariate kinetic analysis the assumption is made that the parameters of the kinetic model are identical for all measurements. This is constrained by the determination of the parameters in a simultaneous analysis of all of the measurements: If the quality of fit of experimental data is insufficient with the given model, the model must be improved through extension to multi-step reaction processes with different combinations.

The task of nonlinear regression is the iterative calculation of the minimum sum of least squares between the experimental data points and the assumed kinetic model. Statistical tests are applied to estimate the quality of the selected model for the description of the investigated process.

The software includes variable import routines for loading data from different type of instruments and methods. Corrections for the transfer function in DSC signals (thermal resistance, time constants) are as well included as the kinetic results can be exported and utilized for thermal simulations (hazards evaluation), controlled rate predictions and temperature program simulations.

References

1 J. Opfermann, G. Wilke, W. Ludwig, S. Hagen, M. Gebhardt and E. Kaisersberger in 'Thermische Analyseverfahren in Industrie und Forschung', VI. Herbstschule Meisdorf 14–18. Nov. 1988, published by Friedrich-Schiller-Universität, Jena 1991, ISBN 3-86007-018-5.

(5) Some proposals for publication of kinetics papers

M. E. Brown, Rhodes University, South Africa

- No papers with kinetic analyses based on experiments done at a single heating-rate should be accepted for publication.
- Authors must assume that readers are reasonably familiar with the background material and not keep

on including 'The Table', etc. Indiscriminate testing of every conversion function should not be reported. Instead attention should be focussed on the possibility of discriminating amongst a selected group of more appropriate models.

- No papers on kinetic studies on fundamentally irreproducible materials, such as sewage sludge, should be accepted for publication.
- Values of E should not be reported and interpreted in isolation from the other members of the kinetic triplet and realistic uncertainties in the calculated values should be reported.
- 'Mechanism' should be reserved for physico-chemical steps and be clearly distinguished from 'kinetic models', 'rate equations' or 'conversion functions'.
- The final test of every kinetic analysis should be to use the parameters determined to construct calculated curves for comparison with the experimental results over a wide and representative range.

(6) Introduction of thermal analysis and kinetics of solid-state reactions into science/technology education

H. Tanaka and N. Koga, Hiroshima University, Japan

The dehydration reaction of solid hydrates usually initiates by a nucleation-and-growth mechanism at preferred sites on the reactant surface. The established reaction is characterized by the existence of a reaction interface, recognized as the zone of locally enhanced reactivity. The overall kinetics are thus determined by the rate of linear advancement of the reaction interface and the geometry of the movement [1, 2]. Such fundamental knowledge on the characteristics of heterogeneous reactions in the solid-state is valuable to all students who will work in the field of material sciences in future. Direct microscopic observations of the textural changes during the thermal dehydration of crystalline hydrates of inorganic salts enable students to understand typical patterns of kinetic behavior that are characteristic of the solid-state reactions [3]. Thermal analysis techniques are also useful for teaching students the thermal behaviors and thermophysical properties of solids [4]. Such educational activities on the thermal analyses and the kinetics of solid-state reactions seem to be important at colleges and universities, as well as at various training courses organized by relevant societies and companies. It is hoped that workers in the field of thermal analyses and kinetics of solid-state reactions will pay more attention to the development of such teaching materials using their expertise.

References

1 H. Tanaka and N. Koga, J. Therm. Anal. Cal., 56 (1999) 855.
2 N. Koga and H. Tanaka, Thermochim. Acta, 388 (2002) 41.
3 H. Tanaka, N. Koga and A. K. Galwey, J. Chem. Educ., 72 (1995) 251.
4 H. Tanaka and N. Koga, J. Chem. Educ., 67 (1990) 612.

Discussion

Yoncho Pelovskii stressed the need to identify whether the reaction being investigated occurred in a single step or was more complex, involving a number of reactions, as well as heat and mass transfer processes. Because of the topochemical nature of solid-state reactions, the initial states of all solid reactants have to be carefully characterized, as well as the partial pressures of all gaseous reactants and products.

Patrick Gallagher commented that when log A and E vary in the same manner, this is most likely a problem of numerical analysis. He queried when the curve-fitting process should stop and put in a plea for the recording of the correct number of significant figures in reported numerical values.

Mike Brown's proposals caused the most discussion. Concern was expressed by E. Illekova that many manuscripts would be rejected on the grounds of an incomplete set of kinetic parameters. Marek Maciejewski explained the impossibility of making kinetic predictions without complete kinetic information. There was considerable discussion (e.g. Hubert Rahier) on what sort of samples would be considered as irreproducible. In the discussion it was pointed out that use of the extent of conversion, alpha, implies that one knows the initial and final states of conversion. Isoconversional methods assume that alpha is independent of heating rate. Mike Reading pointed out that the best way of eliminating this assumption was to use rate-jump or temperature-jump methods. Crisan Popescu gave the interesting example of a hen's egg as an example of a complex sample that would undergo very different reactions under different heat treatments.

There was fairly general agreement that the proposals should be recommendations and not rigid rules. Jean Rouquerol suggested that they should be forwarded to the Editorial Boards of Thermochimica Acta and the Journal of Thermal Analysis and Calorimetry.

The discussion ended rather because of time constraints than through lack of comments and the Kinetics Committee is to consider the proposals.