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Thermal analysis kinetics — past, present and future

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Abstract

The history of the Kinetics Committee of the International Confederation for Thermal Analysis (ICTA) is reviewed. Some of the author's opinions on the development of thermal analysis kinetics over the past thirty years are presented along with his thoughts about areas of future progress.

A SHORT HISTORY OF THE KINETICS COMMITTEE OF THE INTERNATIONAL CONFEDERATION FOR THERMAL ANALYSIS

At the ICTA Council meeting before the 8th International Conference on Thermal Analysis at Bratislava, Czechoslovakia, in 1985, a Science Committee (later Commission) was established under the chairmanship of Dr. Jean Rouquerol. Its purpose was to set up committees in various areas of concern to thermal analysis. Following a very successful Workshop on "Problems of Kinetic Data Reliability Evaluated by Thermal Analysis" [1] at the Bratislava Conference, a Kinetics Subcommittee (later Committee) was formed under the chairmanship of the author. A list of "Topics and Goals to Be Considered" was developed by the Committee members. They included

1. Prepare a yearly committee report to be published in ICTA News.
2. Develop nomenclature, symbols, recommended practices and terms for the description and classification of processes.
3. Develop a list of experts in kinetics to be reviewers of manuscripts submitted to journals.
4. Organize kinetics symposia.
5. Set up tables of derivations of common equations for kinetics models, classification of techniques and methods, etc.

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6 Develop a program to improve quality of kinetics for ICTA members by means of workshops, tutorials, published reviews, etc.
7 Compile kinetics data for solid decomposition reactions.
8 Compile applications to practical purposes, such as thermal endurance test method, service life prediction, hazard analysis, etc.
9 Establish liaison with scientists active in homogeneous kinetics.
10 Organize periodic discussions on reliability of kinetics data.

We will assess the accomplishments of the Committee toward the fulfillment of these goals later in this section.

Many members of the Kinetics Committee met in 1987 at meetings during the European Symposium on Thermal Analysis and Calorimetry (ESTAC-4) in Jena, Germany, and the North American Thermal Analysis Society Conference (NATAS-15) in Washington, USA. There were special invited lectures and symposia on kinetics at these conferences.

A Workshop on Kinetics was held at the ICTA-9 Congress in Jerusalem, Israel, in 1988. Highlights of this workshop which was modeled upon the one at Bratislava are described in a published report [2]. Also, the Kinetics Committee met at this Congress.

Most recently, a meeting of the Kinetics Committee took place at ESTAC-5 in Nice (Sophia-Antipolis), France, on 28 August, 1991. Happily, most of the Kinetics Committee members were in attendance at this conference. These included: H. Anderson, Germany; J. Criado, Spain; D. Dollimore, USA; J. Flynn, USA (Chairman); A. Galwey, UK; K. Heide, Germany; E. Koch, Germany; M. Maciejewski, Poland and Switzerland; T. Ozawa, Japan; J. Rouquerol, France; E. Segal, Romania; J. Šesták, Czechoslovakia; and H. Tanaka, Japan (see photograph). Members of the Kinetics Committee's Working Party on Kinetics Standards and other guests at the Kinetics Committee meeting included: E. Boldyreva, USSR; D. Fatu, Romania; P. Gallagher, USA; N. Koga, Japan; J. Malek, Czechoslovakia; A. Reller, Switzerland, F. Rouquerol, France; E. Urbanovici, Romania; and G. van der Plaats, The Netherlands.

A summary of the items of business and discussions at this meeting gives a fair perspective of the accomplishments of the Kinetics Committee so far.

A working paper on Nomenclature, Symbols and Definitions is being developed from a report by Šesták [3] which is being augmented and amended with terms and definitions from a glossary recently developed by the IUPAC Chemical Kinetics Commission and by other suggestions from the Kinetics Committee membership.

A working paper on Standard Practices and Reporting Kinetics Data by P. Garn has been reviewed by Committee members and is being revised.

The first draft of "An Annotated List of Kinetics Formulae for Thermal Analysis" by E. Segal, D. Fatu, E. Urbanovici and J. Flynn has been completed and is in the process of revision and augmentation.

At the ESTAC-5 meeting. From the left: J. Šesták, M. Maciejewski, H. Anderson, K. Heide, E. Segal and J.H. Flynn.

Some of the results of the Working Party on the Lithium Sulfate Monohydrate Dehydration Kinetics Standards were reported. Dehydration studies on single crystals prepared by V. Okhotnikov, as well as other samples, have been performed by a number of investigators. Reports on the investigation of the kinetics of this system have been published or are being prepared by a number of members of the working party: M. Brown, P. Gallagher, A. Galwey, Y. Masuda, F. Rouquerol, V. Okhotnikov and H. Tanaka. The importance of a combined effort of this type to the progress of thermal analysis kinetics will be discussed more fully below.

The above items discussed at ESTAC-5 cover several of the topics and goals of the Kinetics Committee listed above, namely items 2 and 5: item 2, developing nomenclature and recommended practices; and item 5, setting up tables of equations. Others goals being pursued by the Committee are summarized below.

The Chairman of the Kinetics Committee is also a National Representative on the IUPAC Chemical Kinetics Commission. However no fruitful interaction with the gas phase homogeneous reaction kineticists has occurred thus far. Unfortunately, in this era of great specialization in science, it seems almost impossible to develop transdisciplinary interaction among scientists in differing fields of research.

The development of more stringent refereeing of manuscripts submitted to journals in order to cull out some of the many inferior and more trivial papers on kinetics which occur in thermal analysis literature is also a difficult problem to solve. D. Dollimore and J. Flynn recently had a fruitful discussion with Elsevier Science Publishers on practical ways of improving the manuscript review process. I hasten to point out that the above reference to inferior kinetics papers does not apply to the articles appearing in this volume which are by authors who are eminent in the field. In fact, this outpouring of manuscripts by so many able and dedicated scientists bodes well for the future health and well-being of thermal analysis kinetics.

As described above, kinetics symposia, tutorials, workshops and discussions of reliability of kinetics data have taken place at all recent international thermal analysis conference. A kinetics workshop and a group discussion of the lithium sulfate monohydrate kinetics are planned at the ICTA-10 Congress in Hatfield, England, which will take place in August, 1992. No meetings or conferences devoted solely to Thermal Analysis Kinetics have been organized, because means of funding such enterprises have not been found.

Therefore, only two of the goals listed above have not yet received serious attention from the Kinetics Committee: item 7, kinetics data in solid decomposition reactions; and item 8, applied test methods. The Committee solicits offers of assistance from any scientists who wish to work with us in these and other areas of thermal analysis kinetics.

THERMAL ANALYSIS KINETICS — A BRIEF DISCUSSION OF ITS DEVELOPMENT IN THE PAST THIRTY YEARS AND SOME SPECULATION ABOUT WHERE IT MAY BE HEADED IN THE FUTURE

Past work

If the development of thermal analysis kinetics in the last thirty or so years could be summarized by a single statement it would be that it was the era in which hundreds of cute and clever mathematical manipulations were performed on variations of three (highly stylized) equations.

(a) A rate equation with separable degree of conversion (α) and temperature (T) functions

$$\mathrm{d}\alpha/\mathrm{d}t = f(\alpha)k(T) \tag{1}$$

(b) The Arrhenius equation

$$k(T) = A\ \exp(-E/RT) \tag{2}$$

(c) The temperature integral

$$p(x) = \int_x^\infty (\exp -x)x^{-2}\ \mathrm{d}x \tag{3}$$

where $x = E/RT$.

Unfortunately, all to often, a fourth equation was included
(d) the nth order reaction equation

$$f(\alpha) = (1-\alpha)^n \tag{4}$$

Equation (4) does not generally describe solid state kinetics. Equations (1) and (2) can be applied to some, but certainly not to all, solid state systems. Equation (3) cannot be integrated in closed form and unfortunately, gross and inaccurate approximations for it are used in many of the more popular techniques of kinetic analysis. Thus the analysis techniques based upon these equations have often been used without adequate understanding of their limitations. The resulting misapplication undoubtedly caused and still is causing considerable confusion and misinformation. However, the idea of Šesták's accommodation function to multiply eqn. (4) is worth noting because it somehow generalizes this phenomenological description of solid-state kinetics [4].

Present work

It is encouraging to see a new generation of scientists involved in thermal analysis kinetics who are beginning to question the past years of playing mathematical games with the above equations.

Now that we can "curve fit" and test more complex kinetics models using computer programs, there is no longer a good raison d'être for many of these old approximate equations and techniques. Most certainly all the equations which make gross approximations for $p(E/RT)$ (eqn. (3)) may be discarded. These equations have been shown, a thousand times over, to give differing values for E/R and $\ln A$ from the same data, although they are derived from the same basic equations. The $p(E/RT)$ function can be calculated with simple computer routines to great accuracy. The temperature integral where $x = E/RT$ is

$$p(z) = (AE/\beta R)\int_z^\infty (\exp -x)x^{-2}\,\mathrm{d}x \tag{5}$$

which upon the variable change $x = zy$ becomes

$$\begin{aligned} p(z) &= (AE/\beta Rz)\int_1^\infty (\exp - zy)y^{-2}\,\mathrm{d}y \\ &= (AE/\beta Rz)E_2(z) \end{aligned} \tag{6}$$

$E_2(z)$ is a well-known integral [4]. It is given accurately for values of z greater than two by the continued fraction

$$\begin{aligned} E_2(z) = \exp(-z)(1/z + 2/1 + 1/z + 3/1 + 2/z + 4/1 + 3/z \\ + 5/1 + 4\ldots) \quad (z \geqslant 2) \end{aligned} \tag{7}$$

For values of z less than 2, the series expansion converges rapidly

$$E_2(z) = z \ln z + 1 + (1 - 0.5772156649)z - z^2/2! + z^3/2(3!) - z^4/3(4!) + z^5/4(5!) - \ldots \quad (z < 2) \tag{8}$$

where 0.5772156649 is Euler's constant. A simple computer routine can be set up to calculate $p(x)$ using these two equations.

Therefore all equations using approximations of $p(x)$ such as Doyle–Ozawa–Flynn, Coats and Redfern, Horowitz and Metzger, and Van Krevelen et al. (the first evaluation procedure recently celebrated its 40 year anniversary [6]), etc, may soon be forgotten. In my opinion, also well forgotten are all methods which assume eqn. (4) without careful and meticulous assessment of its valid representation of the isothermal reaction rate.

Future work

Fortunately I can sense a strong current in the direction of ignoring all of these past "foibles" and in looking at thermal analysis kinetics by fresh approaches. Thus I have great expectations for many of the new generation of scientists working in this area, for example, Nobuyoshi Koga, Marek Maciejewski, Jiří Málek, Armin Reller, Vladimir Okhotnikov, Haruhiko Tanaka, and others.

No one can predict the direction in which future research will proceed. However, because the present equations are often inadequate, new approaches must be found.

One direction which appears to hold little promise is that of attempting more general methods for the curve fitting of kinetics data, for example, fitting $f(\alpha)$ and $k(T)$ to power series such as

$$f(\alpha) = a + b\alpha + c\alpha^2 + d\alpha^3 + \ldots \tag{9}$$

and

$$k(T) = A + BT + CT^2 + DT^3 + \ldots \tag{10}$$

Such simplicity is esthetically appealing, but we know that $f(\alpha)$ is often well represented by fractional order or logarithmic terms and $k(T)$ by the exponential. Such dependencies would require many higher order terms in eqn. (9) and (10) and the deconvolution of such a series to the transcendental function would be incredibly difficult.

Therefore, the only other direction is toward the more specific. That is, we must assume that we have to delve deeply into each reaction system to develop tailor-made equations for its kinetics. To illustrate how this might be accomplished, we can hark back to the early work of Max Bodenstein on the hydrogen halides; for example, his work on the gaseous reaction between hydrogen and bromine [7]. As a result of a long and thorough study of this system, he found the rate of hydrogen bromide formation was given by

$$\frac{\mathrm{d}[\mathrm{HBr}]}{\mathrm{d}t}=\frac{k[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{m+[\mathrm{HBr}][\mathrm{Br_2}]^{-1}} \tag{11}$$

Thirteen years later, Christiansen [8], Herzfeld [9] and Polanyi [10] independently developed a free radical mechanism for this reaction whose steady-state solution for the rate of hydrogen bromide formation was

$$\frac{\mathrm{d}[\mathrm{HBr}]}{\mathrm{d}t}=\frac{k_3k_2k_4^{-1}k_1^{1/2}k_5^{-1/2}[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{k_3k_4^{-1}+[\mathrm{HBr}][\mathrm{Br_2}]^{-1}} \tag{12}$$

which was identical in form with the empirical equation of Bodenstein and Lind. This work stands out as one of the landmark achievements of chemical kinetics.

We do not have many Bodensteins these days who have the patience or the freedom to devote years of research to a single reaction system. However, I hope that what the ICTA Kinetics Committee is doing in its lithium sulfate monohydrate working party is the next best thing. That is, having many eminent scientists studying (albeit for shorter periods of time) the same reaction system so that their cumulative effort may match that of a Bodenstein. This project has been under way for only a short period so it is too early to assess its successes (or failures).

One may hope that future studies in solid state kinetics will place more emphasis on looking at a single reaction system with as many differing experimental techniques as are available and varying all the factors which affect its rate individually and, in new ways, to bring out their interrelationship with the other factors to develop a total or "master" rate expression. This should involve the application of all the traditional techniques of thermal analysis (TGA, DSC, TMA, DMA, DETA, etc.), and combining these with FTIR, GC, MS of gaseous products, and microscopic and diffraction studies on the substrate, and so on.

Finally, many of the factor jump and relaxation techniques [11,12] which permit the measurement of the specific relationship between the jumped or oscillated parameter (temperature, pressure of reactant or product gas, etc.) and the reaction rate should be exploited more in the development of the total rate equation. Likewise much greater use should be made of the controlled reaction rate technique of Rouquerol and its complementary utility [13], the stepwise isothermal method of Toft Sørensen [14], and the Quasi-static method of Paulik [15], all of which can expose new relationships between the reaction rate and the factors which affect it, which may not be apparent from the conventional techniques of thermal analysis.

To conclude, I thank Jaroslav Šesták and all my friends who have contributed papers to this special issue, and for this great honor that they have done to me.

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