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Note

Report on the ICTAC Kinetics Committee (August 1992 to September 1994)

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Abstract

This report is a summary of the proceedings at the two most recent workshops of the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC), held at the 10th ICTAC Congress, University of Hertfordshire, UK on 28 August 1992 and at the 6th European Symposium on Thermal Analysis and Calorimetry (ESTAC), Grado, Italy on 13 September 1994. It includes the proceedings of a workshop on the kinetics of dehydration of a proposed lithium sulfate monohydrate standard, reports on the present status of Kinetics Committee working projects, and a summary of the discussion at a workshop on "New Directions for Thermal Analysis Chemical Kinetics".

Report on the Kinetics Workshop at Hatfield

The ICTAC Kinetics Committee held a workshop at the ICTA-10 Congress, University of Hertfordshire, UK, 28 August 1992.

At the start of the Kinetics Workshop, the Chairman of the Kinetics Committee of ICTA, Dr Joseph H. Flynn, was presented with a copy of the commemorative issue of the Thermochimica Acta, Volume 203, prepared in honor of Dr Flynn's 70th birthday by the guest editor, Professor Jaroslav Šesták. The volume contains 44 contributions of major interest to workers in the field of solid state kinetics.

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(a) Kinetics standards: lithium sulfate monohydrate

The first part of the workshop focussed on the progress made in the collaborative study of the kinetics of dehydration of lithium sulfate monohydrate [1,2].

This session was chaired by Professor Patrick Gallagher of Ohio State University, who replaced Dr Andrew Galwey of the Queen's University of Belfast, who had had to withdraw as chairman after undergoing major surgery. The participants requested that the best wishes of the meeting be conveyed to Dr Galwey.

Professor Patrick Gallagher started the session by listing the major requirements for an ideal kinetics standard. After some discussion, these requirements were formulated as:

(1) an irreversible reaction taking place in a single stage, with

(2) a low absolute value of the enthalpy of reaction, so as to minimize self-heating or self-cooling effects;

(3) the temperature range required for reaction should proceed at a slow, but measurable rate, but should not be too low, so as to avoid large temperature calibration errors;

(4) no reaction of the sample with the surrounding atmosphere;

(5) no dependence of reaction on method of sample preparation, pretreatment or particle size and distribution;

(6) the changes to be measured to follow the course of reaction, e.g., mass, amounts of evolved gases, enthalpy change, should be large, so that small samples can be used.

Some of these requirements are not compatible with each other, so compromises would be necessary.

On the above criteria, it was generally agreed that the dehydration of lithium sulfate monohydrate, is *not* a satisfactory reaction, because:

(a) the reaction is reversible at low temperatures, and

(b) is moderately endothermic;

(c) the reaction takes place at temperatures well below 100°C and TG instruments are difficult to calibrate accurately in this range;

(d) rates of reaction are very dependent upon particle-size and prehistory;

(e) overall dehydration involves several rate processes, e.g., chemical reaction, diffusion, recrystallization, and the rate-determining step may not remain the same during the course of experiments;

(f) the overall rate of dehydration is influenced by the presence of water vapor in the surrounding atmosphere.

It was obvious from many comments that the "single crystal standard samples" distributed for collaborative study had not been sufficient and that participants had used their own samples.

Professor Gallagher reported in more detail on the influence of external water vapor on the kinetics of dehydration of samples of powder, pressed pellets, platelet crystals and cubic crystals, studied by means of TG and DSC experiments [3]. Introduction of water vapor into the purge gas (nitrogen) shifted dehydration curves to higher temperatures. The rate of dehydration of pressed pellets lay between that of powder samples (rapid) and crystals (slow). Arrhenius parameters were calculated from TG data, using the Ozawa method. Apparent activation energies varied with extent of reaction, α. Values ranged from 220 kJ mol^{-1} (powder, dry N_2 and low α) to 61 kJ mol^{-1} (pressed pellets, dry N_2, high α). The influence of self-generated water vapor in DSC experiments was pointed out. External water vapor had the least influence of TG experiments on crystals; hence crystals were recommended for kinetic measurements.

Dr Joseph Flynn then reported on results obtained by Professor Yoshio Masuda of Niigata University, Japan [4]. Powdered crystalline lithium sulfate monohydrate, sieved to a narrow fraction of 100–150 mesh, was heated in a Shinku-Riko TGD-5000 RH Microbalance in vacuum (10^{-4} Torr) with a gold image furnace at isothermal temperatures from 70 to 130°C until the degradation was complete. He found that although the dehydration has a simple appearance, the kinetics of the dehydration is not simple and the reaction mechanism cannot be expressed by a single function, $f(\alpha)$. The dehydration mechanism was represented by the combination of A_2 and R_2 functions. The initial acceleratory stage ($\alpha < 0.5$) was described by the Avrami–Erofe'ev A_2 equation indicating a nucleation and nuclei growth process controlled by the diffusion of dissociated water molecules. He postulates that when the two-dimensional phase boundary is formed by the growing nuclei ($\alpha > 0.5$), the dehydration seems to be controlled by the advance of the interface and to have the characteristics of the R_2 model.

Professor Haruhiko Tanaka of Hiroshima University, Japan, who has published very extensively on the dehydration of $Li_2SO_4 \cdot H_2O$ (see references given in Ref. [5]) reported on results obtained by himself and Dr N. Koga in collaboration with Professor Jaroslav Šesták of the Czech Academy of Sciences [5]. Examination of samples showed that the dehydration reaction is initiated by nucleation and growth on surfaces, with complete surface coverage by $\alpha < 0.05$. Cracking produces channels for escape of water vapor. The shape of the advancing reaction front varies with crystallographic direction and this can explain variations in kinetic behavior for different sample preparations. Self-cooling and heat transfer at the reaction front are important factors. Kinetics results for non-isothermal dehydration of single crystals ($0.1 < \alpha < 0.9$) could be described by either the R_n model with $2 < n < 3$, or by the Avrami–Erofe'ev model A_m, with $m = 2$. The most applicable model varies with α, with T and with the compensation effects (KCE) observed, the origin of which is discussed in Ref. [5]. Activation energies calculated for single crystals by the Coats and Redfern method ranged from 272 kJ mol^{-1} (low heating rate, low α) to 78 kJ mol^{-1} (higher heating rate, high α). Nonisothermal dehydration of crushed crystals could be described by either the R_n or A_m models, with different values of n and m for different α ranges and different particle-size fractions. E_a values, calculated by the Ozawa method, ranged from 103 to 154 kJ mol^{-1}.

Professor Michael Brown of Rhodes University, South Africa, briefly summarized kinetics results obtained in collaboration with Dr Andrew Galwey and Professor Alain Li Wan Po of the Queen's University of Belfast, UK [6]. The pressure of water vapor evolved during isothermal experiments in an initially evacuated constant-volume apparatus was measured. The temperature ranges used were 361–402 K for single crystals and 323–363 K for powder (< 150 μm). At 363 K, rate coefficients calculated for the powdered sample were about twenty times greater than those calculated for single crystals. The major portions of the isothermal (α, time) curves were deceleratory and the contracting-volume equation (R_3) gave the best description of the behavior of crystals, and the first-order equation (F_1) fitted the powder data. Activation energies were (106 ± 7) kJ mol^{-1} (crystals) and (87 ± 6) kJ mol^{-1} (powder).

Dr Jean Rouquerol of the CNRS, France, described controlled rate thermal analysis (CRTA) experiments performed by Dr Françoise Rouquerol and himself [7] on the dehydration of $Li_2SO_4 \cdot H_2O$ at a fixed vapor pressure of 0.008 mbar; (α, temperature) curves for constant rate conditions conformed to the A_3 model for single crystals with $E_a = 57$ kJ mol^{-1}, and to the A_2 model for powder with $E_a = 54$ kJ mol^{-1}. The rate jump method gave $E_a = (65 + 9)$ kJ mol^{-1} over the whole range of α.

Dr Klaus Heidie of the Fredrich Schiller University, Germany, also discussed several aspects of the $Li_2SO_4 \cdot H_2O$ dehydration reaction [8].

There was some discussion, led by Professor David Dollimore, University of Toledo, USA, on whether it is possible for any material to be used as a kinetics standard. Professor Dollimore's view was that because kinetic measurements are dependent upon the reaction pathway, and different pathways may be followed under different conditions, the search for a kinetics standard may be futile. Use of a dehydration reaction was particularly unwise and he reminded participants that the effect of water vapor on the rate of dehydration (the Smith–Topley effect) of lithium sulfate monohydrate had been demonstrated by Bertrand et al. in 1974 [9].

The general feeling of the participants was not quite as negative, although the difficulties were recognized. It was felt that the lithium sulfate monohydrate studies had been useful in highlighting difficulties.

(b) General kinetics topics

A short time was available for discussion of more general kinetics topics. Professor Heintz Anderson of the University of Greifswald, Germany [10] supported by his colleague, Dr J. Mentel, strongly recommended the use of non-linear optimization in kinetic analysis. All the differential equations describing the processes involved should be included, i.e., it should be acknowledged that solid-state reactions are multi-step processes, and it is also important that all of the data collected should be incorporated in the analysis and not just selected points, such as peak maxima. Professor Anderson repeated his suggestion [11] that the characteristic temperature (C in the equation, $\ln k = -(C/T) + \ln z$) and the pre-exponential factor Z should replace the use of "activation energy" and "frequency factor" respectively, and that "process exponent" should be used in place of "reaction order", to avoid the implications of homogeneous kinetics.

In closing the Workshop, Dr Flynn speculated on future directions for development of kinetics analysis. He believed that mathematical manipulation of experimental data, in terms of the set of basic equations usually assumed, had reached its limits and that extension of the basic equations might be fruitful. On the question of kinetics standards, he suggested that, in view of the conclusive unsuitability of the dehydration of lithium sulfate monohydrate, as reported in the Workshop, consideration should be given to the possible suitability of the degradation of a (liquid) polymer, or the evaporation of a pure liquid, as a reference process. Added to these suggestions could be the use [5] of the exothermic crystallization of a suitable glass [12–14].

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A business meeting of the Kinetics Committee also was held at ICTA-10. The agenda included:

A report on the Kinetics Committee Meeting at the 5th ESTAC at Nice, France, August 1991, was presented. In addition to the discussion of Kinetics Standards—Lithium sulfate monohydrate studies, other items were discussed. Progress has been made on an Annotated List of Quantitative Relationships for Nonisothermal Kinetics (Flynn, Segal, Fátu, Urbanovici). Working papers on Standard Practices for Thermal Analysis Kinetics (Garn) and Nomenclature for Thermal Analysis Kinetics (Šesták) had been circulated to the Committee members.

Report on the Kinetics Workshop at Grado

The ICTAC Kinetics Committee held a workshop, "New Directions for Thermal Analysis Chemical Kinetics", at the 6th European Symposium on Thermal Analysis and Calorimetry (ESTAC) in Grado, Italy on 13 September 1994.

Dr Joseph H. Flynn (USA), Chairman of the ICTAC Kinetics Committee, introduced the topic by reminding participants of the main developments in kinetics analysis over the last 9 years, i.e., since the formation of the Kinetics Committee at

ICTA-8 in Bratislava in 1985. These developments included movements away from the use of simple "order of reaction" kinetics models, $f(\alpha) = (1 - \alpha)^n$, and crude approximations of the temperature integral, towards the use of a range of kinetics models particularly applicable to reactions of solids, introduction of the accommodation function by Šesták et al., and the generalization and combination of specific equations to allow for the changing mechanism of real samples. He reminded participants of the need to use isothermal experiments for reliable determination of the kinetics function $f(\alpha)$. He also noted that many useful functions had been developed many years ago for describing polymer degradation reaction kinetics.

Professor J. Šesták (Czech Republic) emphasized the need for a broad approach to kinetics, from the very theoretical statistical physical approach to the phenomenological approach used in practical applications. He gave examples of the importance of kinetics of nucleation and growth in fields widely ranging from cosmology, ecology, nuclear energy, pharmacology, biology, medicine (cancer) to cryogenics.

Dr T. Ozawa (Japan) emphasized that new developments in thermal analysis techniques, utilizing multiple techniques such as EGA/MS, and other analytical and microscopic techniques, allowed the mechanisms of reactions to be studied in greater detail and new methods such as non-linear and stepwise heating and CRTA provided different ways of examining the kinetics of reaction.

Dr J. Opfermann (The Netherlands) gave some examples of theoretical modelling of consecutive and competitive reactions with different E_a values for different steps. He showed that resolution of the steps depends upon the choice of an appropriate linear heating rate. The occurrence of different mass losses at different heating rates was a strong indication of the presence of competitive reactions.

Professor P.A. Barnes (UK) gave examples of the use of rate-jump experiments, CRTA and MDSC to separate the kinetics of evolution of each individual gaseous product.

Dr M. Reading (UK) commented that such studies allowed for determination of different mechanisms and noted the use of infrared spectroscopy to obtain additional information.

Professor E. Segal (Romania) stressed the need for the use of low heating rates to obtain reliable kinetics information.

Mr P.P.A. Rossmanith (Norway) stated that kinetics measurements at 5 or 10 K min^{-1} were only useful for comparative purposes to determine if the process is possible and for quality control. Calculations then are not needed.

A discussion developed between Dr Opfermann (The Netherlands), Dr E. Illekova (Slovak Republic) and Dr J. Criado (Spain) about the fitting of kinetics models to thermal analysis curves. Opfermann stressed the need to examine several scans and, possibly, even isothermal results for consistency of applicability of a proposed model. Illekova commented that the parameters of deconvoluted peaks must be tested. Criado commented on the fitting of different kinetics models to different parts of a single experimental curve; then all kinetics models are useful for curve fitting.

Professor H. Anderson (Germany) described the difficulties of correlating the results of experiments on the thermal analysis of calcium oxalate hydrate carried out at several laboratories, in spite of attempts to standardize conditions and procedures. The results could not be compared until after non-linear optimization.

Professor E. Segal (Romania) pleaded for a more positive approach to kinetics analysis in the form of recommendations of what to do rather than of what not to do. He stressed the need for experimental conditions to be specified precisely and the need for the validity of the methods of kinetics analysis uses to be examined critically. The true heating rate, not the programmed rate, is needed. He also questioned the reliability of instrumental heating rates quoted by manufacturers. Also greater precision in temperature measurements is needed for kinetics experiments.

Dr M. Maciejewski (Switzerland), in response to Criado's earlier comments that any kinetics model could be fitted to a thermal analysis curve by adjustment of parameters, reminded the participants that there was only one true mechanism for a process and this had to be found.

Professor J. Šesták (Czech Republic) concluded the discussion by emphasizing the need to take into account both the isothermal description and the topological features of kinetics analysis.