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REPORT ON THE WORKSHOP: CURRENT PROBLEMS OF KINETIC DATA RELIABILITY EVALUATED BY THERMAL ANALYSIS

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I. INTRODUCTION

The workshop moderators (Joseph Flynn, Michael Brown and Jaroslav Šesták) were assisted by a scientific panel, Paul Garn (U.S.A.), Klaus Heide (G.D.R), Erhard Koch (F.R.G.), and Vladimir Logvinenko (U.S.S.R.). Approximately 100 conference attendees participated in the workshop, and these included many scientists who are distinguished for their contributions to this field.

This report of the workshop will include a summary of the "Status Report" presented by J. Flynn (U.S.A.), a resumé of comments made by panelists and attendees during the discussion and also those submitted in writing due to time limitations, and a recapitulation of conclusions and generalizations which emerged about the status of current problems during the above discussions. A related event of the conference, the formation and organizing meeting of a Kinetics Committee in ICTA, also will be described along with some areas which have been suggested for the Committee to direct its activity.

II. SUMMARY OF STATUS REPORT

The workshop opened with a "Status Report" by the Chairman Dr. J.H. Flynn. He commented that although improved thermoanalytical apparatus

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Thermal Analysis Highlights, 8th ICTA, Bratislava, Czechoslovakia.

had led to more reliable and statistically robust data, there had not been a corresponding increase in the reliability of derived kinetic data in that many good attempts to model thermal processes are matched by many other cases of work of poor quality. The selection of a suitable kinetic treatment was still a difficult task, and this was not made simpler by proprietary computer packages in which the algorithm used was not specified and the coding was inaccessible to the user.

Most kinetic treatments are based on solution of linear differential equations which have only tenuous theoretical justification from irreversible thermodynamics where only the first term of a Taylor's expansion about an equilibrium value is used. He also stressed the necessity for more experiments under carefully controlled conditions, rather than more variations of kinetic analysis on one set of data. Attention should be given to carrying out isothermal experiments since it is impossible to separate unequivocally the temperature-dependent and concentration-dependent parts of a rate expression by experiments in which temperature and concentration are changing simultaneously.

Dr. Flynn also suggested that curve-fitting should be done on the differential form of the rate equation now that derivative values can be obtained accurately. This avoids defining initial and final values (integration constants) and the equations are simpler in form. It also avoids the prejudices involved in fitting linear plots.

Turning to the compensation effect, Dr. Flynn commented that over the limited range of E and $\ln A$ values available it was difficult not to find a compensation effect. He suggested that instead of plotting E against $\ln A$, plots of $\ln k$ against $1/T$ for each experiment should be superimposed and examined for intersection at a single isokinetic temperature.

In previous discussions, much controversy had existed over the validity of partial derivatives $(\partial\alpha/\partial T)_t$ and $(\partial\alpha/\partial t)_T$. It was difficult to criticize this when there was so little justification for the use of a linear differential equation in the first place. However, an exact differential should be used to described a state function.

Another point of contention has always been the applicability of the Arrhenius equation to heterogeneous processes. Dr. Flynn commented that there is obviously an energy barrier in heterogeneous reactions and this justifies the use of an activation energy. When plots of $\ln k$ against $1/T$ are distinctly nonlinear, he suggested that k may be being determined from an incomplete or incorrect equation.

III. RESUME OF DISCUSSIONS AND COMMENTS

Dr. Šesták (Czechoslovakia) added some further problems for consideration: the distinctions between homogeneous and heterogeneous kinetics which arise from the presence of structure in the system; the use of non-equilibrium (rational) thermodynamics and the problems of mathematical and statistical analysis, including the use of computers.

Prof. Heide (G.D.R.) asked whether, since thermal analysis was used for solution of technological problems, it was useful to apply basic kinetic methods empirically.

Prof. Jesenák (Czechoslovakia) questioned whether general non-isothermal kinetics or specific reactions should be discussed. Also, recommended error limits for empirical determination of reactions are important. Prof. Anderson (G.D.R.) also stressed that kinetic analysis should only be attempted when the experimental conditions have been carefully controlled to make such an analysis justifiable.

Dr. Várhegyi (Hungary) said that some guidance was urgently needed on which of the many equations suggested for kinetic analysis were actually valid and what sort of extent-of-fit of models to data could be expected.

It was commented that separate equations may be necessary for each reaction and again emphasized that many just want to characterize their materials rather than analyze equations, that a task for the ICTA committee is to determine which equations are correct under which conditions, and that the committee should publish guidelines for how to treat kinetics results.

Dr. Garn (U.S.A.) warned that the usual rate equations do not make any allowance for the surrounding atmosphere. Systems may also range from a polymer glass to a crystalline inorganic powder, hence a wide range of behavior was to be expected. He believed, however, that there was no possibility of finding second-order rate equations for reactions involving solids, and also that the amount of unreacted material should not appear in the rate equation.

Dr. Koch (F.R.G.) suggested that study of non-isothermal kinetics in well-defined homogeneous reactions may lead to better understanding of less well-defined heterogeneous systems where account has to be taken, in the development of models, of factors such as the different phases present and temperature gradients. In correlation results from isothermal and non-isothermal experiments, care has to be taken in allowing for factors such as sample-size, etc. He proposed that the non-isothermal experiments should be carried out at several different heating rates.

Dr. Behnisch (G.D.R.) said that in the field of polymers, agreement between isothermal and non-isothermal kinetic results was generally good and that it was possible to relate *E* values to definite processes. Dr. Flynn (U.S.A.) pointed out that polymers are often studied in the melt and are then homogeneous systems, while heterogeneous systems are far more complex. Dr. Logvinenko (U.S.S.R.) said that there was also a strong correlation between structure in coordination compounds and kinetic parameters. The transition state can be speculated upon in terms of symmetry and distortion.

Prof. Garn (U.S.A.) commented on the Arrhenius model and the problem of collisions in solids. He pointed out that in a solid each atom has many interactions with its neighbors, leading to an almost uniform energy distribution. He posed the question as to whether an example of a reaction could be quoted for which the E value was the same in the liquid and in the vapor phases.

Dr. Tanaka (Japan) suggested that the overall kinetics of a reaction may arise through a combination of models, with marked differences being observed in the behavior of single crystals (including anisotropic behavior) and of powders of the same material.

Dr. Ozawa (Japan) suggested that attention should be directed towards the mathematical derivation of a kinetic relationship, starting from a model of wide applicability.

Prof. Anderson (G.D.R.) pointed out that the simplest real reaction must contain several consecutive steps (including processes such as diffusion) and this must be allowed for any model.

Dr. Vårhegyi (Hungary) queried whether some of the models, e.g., the Avrami–Erofeev equation, were still valid under non-isothermal conditions.

Prof. Jesenåk (Czechoslovakia) stressed that in dealing with powder systems, elaborate statistical treatments would be needed. It is also necessary to measure the physical changes occurring simultaneously with the overall chemical change.

Dr. Adonyi (Hungary) agreed and mentioned as an example the change in surface area which has to be taken into account in determining kinetics of evaporation.

Other problems raised were the appearance of the sample mass in place of conversion in the rate equation by Prof. Anderson (G.D.R.) and the question of the units of k by Dr. Flynn (U.S.A.).

Discussion then centered upon the decomposition of calcium carbonate. Dr. Maciejewski (Poland) asked whether one equation and one set of parameters could be expected for a given compound. The reported values in the literature for the activation energy for calcium carbonate decomposition range from 11 to 915 kcal mol^{-1} depending on conditions. The models which were applied varied and generally no allowance was made for the effect of pressure on the back reaction. Dr. Flynn commented that the process is chemically reversible but not physically reversible and is thus not an ideal system to study and the wide spread of reported kinetic parameters is not unexpected. Dr. Gallagher (U.S.A.) agreed and pointed out that crystallization (exothermic) of the initially formed amorphous CaO is a process which is very dependent upon the nature of the sample, and this process may be easily overlooked when using techniques such as TG.

It was generally agreed that calcium carbonate is not the ideal compound to study, but in reply to a question by Prof. Brown (S.A.) on which type of compound would be most suitable, Prof. Garn (U.S.A.) stressed that the nature of the compound was not as important as being able to specify the conditions completely.

The workshop had to be ended as time ran out and some written contributions were submitted (see enclosure).

It was indeed unfortunate that the workshop discussion was not recorded on tape. The summaries above are based on notes by Drs. M. Brown and R.M. Flynn. They undoubtedly contain some unintentional misinterpretations and omissions. Due to the wide geographical dispersion of the participants and time constraints for the publication of the report, it was impossible to check upon the accuracy of the following summary with each of the workshop members. The authors apologize to those whose contributions may have been misquoted or inadvertently omitted.

IV. RESUME OF PRESUBMITTED CONTRIBUTION

Dr. Kemény (Hungary) points out that the formulation of the rate equation in terms of partial differentials can be shown to be equivalent with the assumption that the same equations hold for iso- and nonisothermal conditions and thus is not applicable to path-dependent systems.

V. ORGANIZATION OF THE ICTA KINETICS COMMITTEE

At the ICTA Council meeting in Liblice, Czechoslovakia, during the week proceeding the ICTA Conference, a Science Committee was established. This Committee, under the chairmanship of Dr. Rouquerol (France), has set up subcommittees in various areas of concern to thermal analysis. A Committee on Kinetics had its organizational meeting at the Bratislava conference and the following scientists have accepted membership on this committee: H. Anderson (G.D.R.), M. Brown (S.A.), D. Dollimore (U.S.A.), J. Flynn (U.S.A., Chairman), P. Garn (U.S.A.), K. Heide (G.D.R.), E. Koch (F.R.G.), V. Logvinenko (U.S.S.R.), T. Ozawa (Japan), J. Rouquerol (France, ex officio), E. Segal (Romania) and J. Šesták (Czechoslovakia). Several other scientists have been asked to become members of the Committee. Since this committee has set up an agenda, acting upon many of the concerns voiced at the above workshop, this tentative agenda is included in the summary and recapitulation of the workshop which follows.

VI. RECAPITULATION OF THE KINETICS WORKSHOP AND GOALS OF THE KINETICS COMMITTEE

The overriding theme of the workshop was the desperate need for setting up guidelines for kinetic models, equations and techniques. However, the specific problems which should be attacked and the means to be used in their resolution varied according to the area of interest of the panelists. It was agreed that in most work found in the literature, experimental and procedural variables are not defined well enough, experimental techniques are too limited, and kinetic models and equations are oversimplistic. It was also generally acknowledged that many of these problems are inherent in the complex heterogeneous nature of the reactions investigated in thermal analytical studies.

Several dichotomies among the viewpoint of the panelists manifested themselves during the discussion. One was the need for differing philosophies for kinetic analysis for, on the one hand, those engaged in basic theoretical research and, on the other hand, those interested in quality and production control, failure prediction, etc.

Another area of difference is based upon the nature of the substrates of interest to the investigators. This second dichotomy appears upon comparing TA of inorganic with polymeric materials. Most inorganic systems have their atoms held in rigid matrices. When they react, it often involves cooperative phenomena or phase changes. Low molecular weight products are formed at temperatures near the equilibrium temperature so that reactions are reversible. The reactions involve gaseous evolution so that TG is the common analytical technique. Heat and material diffusion gradients result and the remaining solid forms a new physical state. All of these factors lead to systems which are very dependent upon pressures of product gases, geometry, rates of material and thermal diffusion and various procedural variables. On the other hand, organic and especially polymeric materials are more sluggish kinetically. For example, polymers usually do not degrade at measurable rate until they are heated to about 100°C above their equilibrium or ceiling temperature, so the reactions are irreversible. Polymers are often in the liquid state at reaction temperature, and even below their glass transition temperatures there can be considerable movement. Therefore, in spite of cage effects, conditions can usually be found where reactions are slow enough that thermal and material diffusion are not rate-limiting. As a result, meaningful kinetic models have been developed for many of these systems. Also, many types of reactions–polymerization, depolymerization, oxidation, and even phase changes such as glass transitions—can be investigated kinetically by many different TA methods.

These differences in basic philosophies and material systems must be taken into account in the development of guidelines. The members of the Kinetics Committee were fresh from the panel discussions when they had their organization meeting so the tentative agenda of goals to be considered, which is listed below, reflects their awareness of the many problems facing thermal analysis kinetics which were defined and discussed at this very fruitful and successful workshop.

This list is growing as the new committee members submit their ideas about the proper aspirations for the committee. The Kinetics Committee

TABLE 1

Topics and goals to be considered by the ICTA kinetics committee

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 ICTA Kinetics Symposia.
5. Set up tables of derivations of common equations for kinetics models, classification of techniques and methods, etc., to be referred to by authors (rather than lengthy "rediscovery" in journal articles).
6. Develop a program to improve quality of kinetics for ICTA members by means of workshops, tutorials, published reviews, etc.
7. Compile kinetic data for solid decomposition reactions.
8. Compile applications to practical purposes, such as thermal endurance test methods, service life prediction, hazard analysis, etc.
9. Establish liaison with scientists active in homogeneous kinetics.
10. Organize periodic discussions on reliability of kinetics data.

solicits comments from all thermal analysts concerning the appropriateness of the above items and suggestions for other areas which might be added to the agenda.

PROBLEMS OF THE RELIABILITY OF KINETIC DATA EVALUATED BY THERMAL ANALYSIS

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It is well, known that the physical meaning of kinetic data obtained by thermoanalytical techniques is open to discussion, as confirmed at the ICTA '85, Conference and the workshop on the reliability of kinetic data in particular. It was indicated by some speakers that 75% if not 100% of thermoanalytical kinetic information is meaningless. If the situation is really so dramatic, then what is the reason, and why are thermoanalytical methods so widely used for kinetic studies in different countries?

Before discussing whether it is useful or not to apply a particular method, it is necessary to know what the aim of the study is. So, first of all, we should come to a conclusion as to why we need kinetic data.

The only argument in favour of nonisothermal kinetic measurements is their rapidity compared with isothermal kinetic studies. Thus, if we need kinetic information for some practical, e.g., technological, purposes, the rapidity of thermoanalytical techniques may be a sufficient advantage to compensate for the absence of a physical meaning of the kinetic parameters obtained. Certainly, the data must be easy to reproduce and to control.

However, if the aim of the study is to obtain some fundamental information on the physics and chemistry of the reaction, then what is the use of acquiring rapidly some data with no definite physical meaning?

It is a common argument of those who do apply non-isothermal kinetic techniques for fundamental studies that it is necessary in each instance to compare the data of a non-isothermal kinetic study with the isothermal kinetic data, and in such a way to ensure that non-isothermal methods are applicable in a particular instance. It is even better to study also kinetics, using single crystals and definite faces of single crystals. However, if such a major task is still unavoidable, then why is it necessary to apply subsequently a non-isothermal technique, the only advantage of which is its rapidity?

As far as fundamental science is concerned, why are kinetic parameters (whatever method is used to obtain them) necessary? Sometimes an answer can be heard: "I study kinetics to establish the mechanism of the reaction". However, it is well known that studying kinetics is not the quickest way of understanding the mechanism of a solid-state reaction.

There are many difficulties arising from the fact that a solid-state reaction can be reversible and can be accompanied by structural changes and diffusion processes. However, even if we consider the simplest possible case, i.e., an intrasphere ("intramolecular") solid-state isomerization not accompanied by a structural transformation, we shall see that the kinetics of such a reaction may be far from the kinetics of the same isomerization in solution. At least two reasons for such a "deviation" ("abnormality") may exist: (1) the initial non-equivalence of different complex ions in a real crystal as regards their reactivity and (2) the autoinhibition of the reaction by the product formed. No kinetic study can help us to distinguish between these two possibilities. Only a direct study of the distribution of the complex ions in terms of their reactivity in the initial crystal and a direct study of the inhibiting effect of the product on the reaction can prove one or another hypothesis.

When a solid-state reaction is studied, the first step is to use direct methods to clarify the mechanism of the reaction at a qualitative level. Only then may a kinetic study follow to give some quantitative information, permitting some predictions to be made. This is the sequence of steps when any method of kinetic analysis of a solid-state reaction is used. To obtain kinetic data with a clear physical meaning, it is necessary first to study the mechanism of the solid-state reaction at a qualitative level.

It is clear that if we need kinetic parameters to make our knowledge of a mechanism more precise, the data should be correct and have a clear physical meaning, otherwise any information obtained by a direct method will be more valuable than the kinetic data. It is well known that the problem of obtaining correct kinetic data for solid-state reactions is very difficult. Nevertheless, some progress has already been achieved in this field. It was shown, for example, that isothermal kinetic studies are the only ones suitable for fundamental purposes. This does not mean, however, that any isothermal kinetic study is good and gives correct data. The problem is more complex. This area is being intensively studied in many countries (and at our Institute).

The main ideas expressed here are the following:

(1) Methods of thermal analysis are good when they are used for practical (e.g., technological) purposes. For example, if a technology requires non-isothermal conditions, then non-isothermal kinetic methods can be used to characterize the process and improve its technological parameters.

(2) The methods of thermal analysis are very fruitful for direct studies of the mechanisms of solid-state reactions, but only if the methods themselves, and not the non-isothermal kinetic analyses based on these techniques, are used.

(3) Non-isothermal kinetic studies are useless for understanding the physics and chemistry of solid-state reactions, as the meaning of the kinetic data obtained is vague.

NEED FOR STANDARDIZATION OF THERMOANALYTICAL KINETIC COMMUNICATIONS: TERMINOLOGY SUGGESTIONS

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In the recent thermoanalytical literature, at least one quarter of the articles deal in some way with kinetics. Comparing them with each other, we can easily recognize frequently repeated paragraphs or introductions that regularly reproduce certain equations (e.g., rate laws, Arrhenius constants) and theoretical or evaluation sections listing, e.g., equations of integral models for describing various rate-controlling processes. Although there is a certain value in becoming involved in these kinetic problems, it is of real help only for beginners and is unnecessary for advanced workers, simply taking up unnecessary space by presenting already well known information. It follows that, for the sake of more uniform presentation, we need some standardization in order to reduce the length of articles without sacrificing understandability. Thus we need to formulate a standard kinetic nomenclature and to clarify the meaning of individual terms.

In the following text the most appropriate terms are listed for initiating a discussion of kinetic nomenclature.

Process. Occurrence accompanied by the change in a certain physical property of the sample.

Reaction. A process accompanied by a change in chemical composition.

Homogeneous process. A reaction in which neither the number of the initial stoichiometric phases nor their chemical composition is changed.

Heterogeneous process. A reaction in which the original amount of chemical phases or their macroscopic composition is changed, accompanied by the formation, disappearance or shift of phase boundaries. It can further be classified according to whether it is accompanied by a change in the sample mass: *evaporation* or *sublimation* (when the formation of a volatile phase does not lead to a change in the composition), *decomposition* or *recombination* (in which the formation or disappearance of a volatile phase leads to the creation of a new conservative phase). Processes without a change in the sample weight are generally termed:

Solid-state process. A reaction that involves phase *transition, decomposition* and *synthesis*, where the initial conservative phase changes, diminishes or grows, respectively.

Catalytic process. Takes place at interfaces whose shape, size and reactivity remain unchanged during the reaction considered.

First, broadened, second-order and glass-phase transitions. These exhibit the change, continuity and quality of the value of an extensive property at the point of its transition, the last one being understood as non-equilibrium.

Rate law [$\dot{\alpha} = \mathrm{f}(\alpha, T, \ldots)$]. A constitutive equation expressing the rate of the process, proportional to the independent functions of parameters characterizing the state of the sample valid in the simplest specified form as $\dot{\alpha} = k(T)\mathrm{f}(\alpha)$.

Degree of conversion (α). Understood as a dimensionless ratio $[Z(t) - Z(0)]/[Z(\mathrm{F}) - Z(0)]$, where Z is the measured physical property selected to represent a process in question at the instantaneous (t), initial (0) and final (F) stages.

Rate of the reaction. The time derivative of the degree of conversion $\dot{\alpha} = \mathrm{d}\alpha/\mathrm{d}t$.

Equilibrium advancement of the reaction (λ_{eq}). This is the degree of reaction that would be attained at infinitesimal time if the given temperature of the surroundings is maintained constant.

Isothermal degree of conversion (α). The degree of conversion determined for time t at constant temperature T.

Non-isothermal degree of conversion (λ). The degree of conversion, determined during TA experiments at constant heating rate, and equal to the isothermal value for invariant processes (thus being effective only for variant processes).

Invariant process. A reaction where the equilibrium advancement changes stepwise from 0 to 1 at a single temperature T_0 called the equilibrium temperature of the first-order transformation.

Variant process. A reaction where λ_{eq} changes continuously within a certain temperature interval from T_0 to T_F.

Equilibrium background of the process [$\lambda_{eq}(T)$]. The temperature dependence of the equilibrium advancement effective for variant processes.

Kinetic model. An analytical function expressing the time development of α in the differential [$f(\alpha)$] or integral [$g(\alpha)$] mode.

Integral kinetic models. Mathematical equations describing the individual rate-controlling reaction valid for diffusion (D), interface chemical reaction (R) and nucleation growth processes (G or A).

Reaction order (n). An effective power exponent of the formal function $(1 - \alpha)$ derived for a homogeneous-like reaction in the derivative mode.

Power exponents (n, m, p). Effective exponents in the formal description of heterogeneous reactions using equations valid in derivative modes: $(1 - \alpha)^n\alpha^m$ and/or $(1 - \alpha)^n[-\ln(1 - \alpha)]^p$.

Arrhenius rate constant [$k(T) = A_0 \exp(E/RT)$]. Describes the frequency attempts (A_0) to surpass an energy barrier (E) of the reaction, the exponential expressing the probability of successful attempts for thermally activated processes.

Activation energy (E). Experimentally determined constant, usually understood as overall (apparent) activation energy consisting of the sum of partial (elementary) energies for nucleation (E_N), crystal growth (E_G) and diffusion (E_D).

Kinetic compensation effect. Apparent interdependence between E and A_0, usually expressed as their linear dependence.

Evaluation procedure. A mathematical treatment of experimental data in which the kinetic model (power exponents) and Arrhenius rate constants (E and A_0) are determined by the following methods:

Variables	Model function	Rate constant	Name of method
α, T	$g(\alpha)$	$\int k(T) \Rightarrow p(x)$	integral
α, $\dot{\alpha}$, T	$f(\alpha)$	$k(T) \Rightarrow A_0$, E	differential
$\Delta\alpha$, $\Delta\dot{\alpha}$, ΔT	m, n or p	$\Delta k(T) \Rightarrow E$	difference-differential
α, $\dot{\alpha}$, $\ddot{\alpha}$, T, $\dot{T}$	$\frac{df(\alpha)}{d\alpha f(\alpha)}$	$dk(T)/dT$	double-differential
α or $\dot{\alpha}$ const.	–	E, A_0	sectional
$\alpha_{0.5}$, $T_{0.5}$	$f(0.5)g(0.5)$	E, A_0	half-time

Kinetic data accuracy and correctness. Ability to determine numerical values with a given accuracy and to find a correct coincidence between the mathematical model applied and the actual process investigated.

Thermal modes of investigation. Isothermal (T = constant, $\dot{T} = 0$); linear non-isothermal ($\dot{T}$ = constant = β); hyperbolic non-isothermal ($\dot{T} = \beta T^2$); general non-isothermal [$\dot{T} = f(T)$]; (e.g., exponential non-isothermal); self-generated non-isothermal [$\dot{T} = f(T, \alpha, \ldots)$].

Thermal modes of enthalpy changes indication. Spontaneous thermal fluxes are measured on the basis of a well defined thermal gradient while mere temperature differences are measured by *thermometry. Compensation thermal fluxes* are measured as the energy (heat supply) necessary to maintain the specimens at the required (balanced) temperature.