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STOCKTAKING IN THE KINETICS CUPBOARD[*]

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Some of the continuing problems of kinetic analysis of solid-state reactions are reviewed and some recent advances towards their solution are discussed. Attention is drawn to the important findings of an ICTAC Kinetics Project that need consideration by authors and editors of kinetics papers.

Keywords: *kinetic analysis, solid-state reactions*

Introduction

In every issue of the major journals in Thermal Analysis, and scattered in other related journals, papers deal, in various depths, with kinetic aspects of the thermal behaviour of materials. Many of these papers fail to take into account some important developments in this controversial and confusing area of research. Progress in this area definitely requires some stocktaking and some spring cleaning. The figurative 'cupboard' of the title, could be as real as the collections of reprints and photocopies collecting dust in offices and laboratories, or the files filling up the storage space on hard drives. How much is worth keeping?

An attempt was made in 1996 to identify some of the major areas of controversy in a paper entitled : 'Steps in a Minefield: Some kinetic aspects of thermal analysis' [1]. These included:

- the quality of information from isothermal *vs.* non-isothermal experiments
- the validity and interpretation of Arrhenius parameters
- the significance of the Kinetic Compensation Effect
- the blurring of the meanings of 'mechanisms' and 'models'

Since that date, some of the important advances have included:

- the ICTAC Kinetics Project [2–6]
- the emphasis on isoconversional methods [4, 7]
- Burnham's distributed activation energy model [8, 9]
- L'vov's 'Physical Approach' [10, 11]
- Korobov's Planigons [12]
- Galwey's rather pessimistic reviews [13–16]

Progress report

By now there is fairly general agreement that both isothermal and non-isothermal approaches have their advantages and disadvantages and that an ideal study would include comparison of data obtained from both techniques thus indicating the reliability of the measurements and/or revealing their complexity. An interesting development is the Serra, Nomen and Sempere non-parametric approach (NPK) [17, 18] which uses matrix techniques to convert non-isothermal data into the equivalent, expected isothermal data. Sewry and Brown [19] and Heal [20] have explored this interesting method of analysis.

Although Laidler's excellent papers [21, 22] have not received the attention that they deserve, they show clearly that attempts to find alternative functions to describe the temperature dependence of the reaction rate coefficient in homogeneous reactions are unlikely to be fruitful, so the simple form of the Arrhenius equation is generally used. The validity of extending this Arrhenius treatment to heterogeneous reactions has long been debated [23] and it is generally agreed that interpretation of the parameters derived cannot closely follow the examples of homogeneous kinetics.

Too much emphasis has been put on determining (and interpreting) the activation energy in isolation. This is the equivalent of solving only one of three unknowns in a set of simultaneous equations. Attempts to correlate activation energies with the breaking of particular bonds in a transition state, have not been very successful in homogeneous kinetics, and are even less successful in reactions involving solids. The importance of obtaining at least one full kinetic trip-

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let, E, A and the conversion function, to describe a rate process, cannot be overemphasized. Most reactions involving solids can be expected to be complex combinations of rate processes. Even in the so-called, and highly recommended, 'Model-free' methods of kinetic analysis, which include temperature or rate jump methods [24] and modulated temperature programmes [25], elimination of the model (or conversion function) can only be temporary [19]. Maciejewski [3] and Maciejewski and Reller [26] have given some of the clearest demonstrations of the unreliability of predictions of the extent of reaction made using the wrong conversion function.

The Kinetic Compensation Effect (KCE) continues to attract interest in spite of the paper by McBane [27] who clearly pointed out the dangers of finding meaningless correlations between some sets of data and the criteria that need to be satisfied before behaviour can be described as isokinetic. Brown and Galwey [28] reported on the apparent compensation effects found in the results of the ICTAC Kinetics Project [2] where the same data sets were used by the different participants.

Mechanisms and models

The lack of consistency in the use of the terms 'mechanism' and 'model' continues to cause unnecessary confusion [13]. In homogeneous kinetics the generally accepted use of 'mechanism' is to describe the chemical steps by which the overall reaction occurs and this leads to the concept of molecularity.

In heterogeneous kinetics, one of the important models for reaction is based upon the geometrical processes of nucleation and growth. Different geometries of both processes lead to a variety of mathematical relationships (conversion functions) describing the course of the overall reaction. For example, nuclei may be formed linearly with time and grow uniformly in three dimensions. Agreement of the experimental data (α, t or α,T), measured using a non-specific technique such as TG or DSC or even evolved gas analysis of specific gases, with the predicted relationship for such a model, does not provide evidence that the reaction actually occurs via a nucleation-and-growth model. Visual observation, using optical or electron microscopy, as well illustrated in some of the studies by Galwey and colleagues [29] and in the classic study by Wischin [30] can provide support for such a model. Even if such a physico-geometrical model does describe the observations, the chemical steps involved in the formation and growth of the observed nuclei will generally require further investigation, if they are accessible et all.

As another example, experimental data may appear to be described adequately by one of the models based upon diffusion in one, two or three dimensions, but rate control by diffusion has to be proved by complementary experiments and formulation of the mechanism requires the identification of the diffusing species.

Reverting to homogeneous kinetics, one could, for example, identify the experimental data as being described by a reaction-order (RO) type of rate equation. The question then arise as to whether this rate equation applies to the overall reaction occurring in a single step, or by a mathematical combination of the rate equations for a series of individual steps, or represents the rate equation applicable to the rate-determining step (rds) only, without providing information about the rates of faster steps. In certain favourable instances one can draw conclusions from the RO model regarding the possible molecularity of the steps concerned, but even this is still a step away from identifying the molecules involved.

The well known and over-published Table [31] containing collected relationships that have been found useful in describing the course of various solid-state reactions, has been rightly criticized for being too limited. However, distinguishing which, if any, of this limited set of conversion functions applies most closely to given experimental data is not a trivial problem, even after isoconversional methods have been used to temporarily eliminate this member of the kinetic triplet. More-realistic models, involving multi-step processes known to be influenced by factors such as crystal structures, crystal defects, etc., that are extremely difficult to quantify, are likely to lead to complex conversion functions containing many parameters that are difficult to measure independently. Even if such relationships are developed, are experimental data, obtained by non-specific techniques, likely to be sufficiently accurate and repeatable to justify the effort? Even in homogeneous kinetics, the rates of many reactions that have been shown by sophisticated spectroscopic and other independent methods to be of considerable complexity, are approximately describable by relatively simple rate equations. With the use of the complementary evidence it is then sometimes possible to rationalize the applicability of the rate equation, but the reverse process of discovering complexity from kinetic measurements is less fruitful.

The definition of the extent of reaction (α)

On the reasonable assumption that the real processes involved in the thermal decomposition (crystolysis) of even the 'simplest' of solid reactants are more complex than allowed for in the traditional models, one is faced with the problem of defining the extent of reaction, α, upon which the validity of the conversion function, in whichever form used, $f(\alpha)$ or $g(\alpha)$, depends. Use of isoconversional methods does not avoid this problem. Even if data were available for the rates of evolution of each of the gaseous products and it could be assumed that no secondary reactions between gases, or between the gases and the solid residue, had occurred, one would have to examine this data carefully for evidence of multi-step processes and it is possible that concurrent processes in the solid residue, such as recrystallization, could affect this evolution indirectly.

In the literature there are several examples of studies done on the thermal behaviour of exceedingly complex and irreproducible reactants, for example sewage sludge, coals, crude oils, etc. Whether it serves any purpose to attempt to extract kinetic information from such studies is extremely debatable. At best, any kinetic parameters derived could only be regarded as empirical coefficients for compact description and comparison, from sample to sample within an industrial laboratory, of the thermal behaviour of that particular sample.

A further controversial issue is related to the concept of a 'variable' activation energy [16, 32, 33]. Use of isoconversional methods can produce plots of the activation energy *vs.* the extent of reaction, α. Variation of E_a with α is generally taken as an indication that the reaction is complex and that α needs redefinition to account for the complex steps.

The ICTAC kinetics project

The variability of experimental data obtained for solid-state decompositions is a cause for considerable concern [34]. Different batches of the reactant can behave differently under apparently identical conditions and experiments on the same batch of reactant under slightly altered conditions can produce very different results. This is particularly true for reversible decompositions where changes in the rate of removal of volatile products can affect the overall rate of decomposition.

In an attempt to eliminate some of the experimental variables and to focus instead on the variations in kinetic parameters arising from methods of kinetic analysis, several sets of numerical data were provided (both isothermal and programmed temperature) to participants in this project. They were invited to use their favourite methods of kinetic analysis to determine the kinetic parameters. Although some of the data sets were obtained experimentally so that no 'true' kinetic parameters were available as a benchmark, one set was data simulated for a complex reaction involving two parallel first-order (F1) processes with equal weighting: ($A_1=10^{10}$ min^{-1}; $E_1=80$ kJ mol^{-1}; $A_2=10^{15}$ min^{-1}; $E_2=120$ kJ mol^{-1}). The data, methods, and results are described in Part A of the project report [2]. The main methods of kinetic analysis used by the contributors were nearly all isoconversional methods [4] and included: the Flynn, Wall and Ozawa (ASTM E698); the Kissinger, Friedman, Freeman and Carroll, Modified Coats-Redfern and Non-parametric methods [17, 18]. The kinetic triplets obtained are listed in tables. Comparison of pre-exponential factors was sometimes not straightforward because of uncertainty regarding units and accumulation of terms in what is often the intercept of linear regression. The Project demonstrated that there is ample computational machinery available for testing the 'goodness-of-fit' of experimental data to the limited set of kinetic equations. However, the goodness of fit is only the necessary, but not the sufficient condition for the identified reaction model to be physically sound. Introduction of additional kinetic parameters can only be justified by physical significance and not simply by improvement of the goodness of fit.

Methods of kinetic analysis are not in competition with each other. Provided that the methods are computationally sound, they should provide increased confidence in the resulting parameters.

There is a definite need for a shift of emphasis from computational aspects of kinetic analysis to better planning of experiments to reveal details of the important bond redistribution processes leading to new compounds and/or new structures and the difficulties of interpretation of results. There is a need for development of models for multi-step solid-state processes and for studies that probe how factors such as melting, sublimation, diffusion, adsorption, sintering, crystallisation, etc., may control solid-state reactions.

L'vov has published a lot of controversial papers on what he has named his 'physical approach' [10, 11]. This approach is based upon the assumption of an initial step involving evaporation of the reactant, e.g.:

$$CaCO_3(s)\to CaCO_3(g)\to$$
$$CaO(g) + CO_2(g)\to CaO(s) + CO_2(g)$$

This is an interesting idea, which could be well applicable to a limited number of reactants, but its extension as a general mechanism covering all solid-state decompositions appears to conflict with two principles of Philosophy, namely, Occam's Razor, which requires that no more assumptions than are necessary should be made; and attempts to explain everything in terms of one principle, e.g. early Greeks 'all is water' and today's TOEs (theories of everything). There is a need for a critical assessment of these suggestions that takes into account the adjustable parameters introduced and the complex mixture of kinetic and thermodynamic concepts.

Korobov [12] has tackled the difficult but essential problem of trying to introduce the influence of the crystal structure into models describing the decompositions of solid reactants. He illustrated this approach using the thermal decomposition of NH_4HCO_3. As a start he assumed that there were no surface imperfections and that the reaction started by proton transfer from the NH_4 tetrahedron to an oxygen atom in the HCO_3 group as the result of a fluctuation. The reaction interface then advances by covering of a plane by identical shapes (planigon tessellation). From experiments, nuclei are seen to form at the (001) crystal face and when reaction has had time to proceed into the bulk, rhombic holes are observed. Projections of the NH_4HCO_3 crystal structure onto the (001) face are given and the interactions between conjugated NH_4 – HCO_3 pairs are described. This brave approach deserves commendation although this example applies to perfect single crystals of a reactant which leaves no solid product. Will it prove possible to allow for the presence of defects of various kinds that are known to influence the initial nucleation steps in many reactants, and can the approach be extended to the more 'traditional' crystolysis model resulting in a solid residue: $A(s) \rightarrow B(s)$+gases. Such an extension would also have to account for the differences between topotactic decompositions, where the structure of B(s) is related to that of A(s), and the formation of non-crystalline residues.

Conclusions

What can we throw out of our overcrowded cupboard? No papers with kinetic analyses based on experiments done at a single heating-rate should be accepted for publication. There is mathematical machinery available [2] far in excess of the requirements for handling the limited quality of most experimental data. 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.

The same restriction on publication should apply to kinetic studies on fundamentally irreproducible materials such as sewage sludge. There are sufficient problems remaining to be solved regarding the limited kinetic reproducibility of nominally pure reactants.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.

Development and testing of rate equations for multi-step processes [8, 9] is going to require much more chemical information, e.g. evolved gas analysis on individual gases. Each reaction step in a complex process must be clearly defined so that alpha is also properly defined.

'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. Such a construction requires knowledge of all the kinetic parameters.

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