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STRATEGIES IN NON-ISOTHERMAL REACTION KINETICS

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At the 8th ICTA in Bratislava, stimulating discussions were started on kinetic data reliability [1] and computer application [2]. Aspects of this discussion were reactivated during ESTAC 4 in Jena, both in the final session on solid-state reactions, and in the subsequent session of the ICTA Kinetics Committee, established in Bratislava. As a member of this committee, the author would like to use this opportunity to make some remarks on data-evaluation, based on his general experience on reactions in solution rather than on his theoretical studies on heterogeneous mechanisms.

Kinetic data and evaluation strategies

Despite the present pessimism concerning the true meaning of kinetic data calculated from solid-phase experiments, most kineticists agree on the statement that mathematics must be the element responsible for the nature of the kinetic effects studied. However, even in some simple homogeneous mechanisms, to time-resolved algebraic expressions exist for the rate, and thus the general question arises as to whether it is an effective concept to use the often approximate analytical equations valid for a certain assumed reaction mechanism, especially in the early stage of an investigation.

On the other hand, kinetic data, such as rate constants or activation energies, must be representative of a particular reaction step, but not necessarily of the total reaction. Even very accurate data, obtained from the total plot, are often meaningless when several chemical or physical steps are involved in the total process. Therefore, such data must vary when estimated over different periods of the reaction.

Hence, it is obvious that during a period of increasing data-processing techniques, the development of appropriate strategies for model searches and data-evaluation seems much more important than the determination of more accurate data, e.g. activation parameters, but restricted to the fixed idea of a mechanism. It is

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true that much commercial equipment is not capable of yielding sufficiently accurate kinetic data, because the reproducibility is too poor. However, the reliability of reaction-coupled data is also a function of the prevailing mechanism, so that even a bad apparatus may help to solve a kinetic question satisfactorily.

The opinion of the author is that the following sequence of steps is a promising strategy for kinetic studies:

1. The use or development of equipment which allows the distinction of apparatus factors from chemical or physical information on the sample. (Solutions: stirring and internal temperature measurement; solids: correction tables for the influence of sample weight and size, temperature deviations, etc.)
2. The performance of experiments with linearly increasing temperature.
3. Routine evaluation using the simplest access possible, assuming a one-step process.
4. A discussion of the deviations of adequate data from their reference values attributable to elementary processes or situations (pattern-recognition methods).
5. In order to attain sufficient information on the system, the performance of experimental series where one condition parameter is changed (reactant concentration(s), added diluent, heating rate, sample weight or packing density, pressure).
6. If possible, the use of non-linear temperature programs.

Homogeneous reaction kinetics

For mass-action kinetics, the author has proposed the use of apparent activation data as reference, obtained by a least square fit for stage 3, and, after the correction of the shape index and half-width via DTA, to use his mechanistic diagram for the determination of the best model. On the basis of concentration and/or heating rate series, pattern recognition can already be used through a comparison with evaluated theoretical plots of two-step models [3]. In mass-action kinetics, multi-step reactions may be systematically built up by appending a further step at different locations in the respective n-step model. Thus, an automatic kinetic analysis should be attainable which requires computer strategies similar to those used in a chess-computer [4]. In studies of the oscillating Belousov–Zhabotinsky reaction by DTA and UV spectroscopy [5], the author could demonstrate that the agreement of any assumed model, such as his nine-step model, with that concealed in the experimental plots may be tested by an adequately defined valuation number. This is derived from the degrees of coincidence of 3–5 behaviour types of adequate parameters in all optimized intervals of the starting concentrations of the reactants used in the respective series.

The occurring behaviour types are fixed by kinetic parameter codes, leading to a new kinetic fingerprint method, which utilizes kinetic plots generated by integration programs for many models. Progression from n-step to $(n+1)$-step models enables one to study the characteristic extensions of such codes, which is the prerequisite for a systematic kinetic analysis. As the author revealed in another contribution at this conference [5a], simultaneous discussion of the correlation coefficients of Arrhenius fits with the mechanistic coordinates makes this strategy even more specific.

Heterogeneous reaction kinetics

In solid-state kinetics, the access to a reaction mechanism is strongly barricaded by diverse problems, and there is much criticism concerning the usefulness of a non-isothermal kinetic approach (e.g. [6]). Part of these barricades may be removed by an adequate construction of equipment (stage 1) and the planning of adequate series (stage 5), but a systematic classification of heterogeneous kinetics is hard to achieve, since a disintegration into elementary steps seems mostly unattainable and the concept of concentration unfounded, e.g. for solid polymers.

The classification method of Sharp et al. [7], using master-diagrams, has also given much impetus to non-isothermal studies. However, only a single rate constant is considered here, which concerns more than 20 mechanisms with extremely different rate laws, presented by the function $g(\alpha)$. The author has calculated the corresponding isolated characteristic regions in the mechanistic diagram [3], but he is aware of the fact that these include only a small fraction of the mechanisms really expected; usually, a sophisticated network of chemical and physical processes will be present. Therefore, he agrees with Anderson, Heide, Oswald, Seifert and many others as to the conclusion that other techniques than the rather kinetic DSC, DTA or TG should also be used, such as thermomicroscopy oz X-ray analysis. Nevertheless, a satisfactory agreement of a signal with one of the $g(\alpha)$ functions, which reveals the corresponding activation parameters as constant over the whole range of the fractional conversion and independent of the condition parameters, would indeed justify the suggestion that the respective mechanism is formally valid.

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