

THE RATE LAW OF N TH-ORDER IN THERMAL ANALYSIS

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ABSTRACT

The kinetics of only a small portion of heterogeneous reactions may be described by a rate law of n th order. Problems, but also successful applications of this rate law—mostly used in isothermal thermoanalytical experiments — are discussed. A general comparative evaluation strategy is proposed which is based on the results stemming from the assumption of a fitted one-step reference process, and aimed at the type of reaction mechanism involved. Due to the type of this mechanism, typical changes of the mechanistic coordinates, available from peak asymmetry and half width, and of other quantities are to be expected. The procedure was examined both by using DTA curves and non-isothermal curves of the optical extinction in solution. It should also be applicable to problems in heterogeneous kinetics.

INTRODUCTION

It is well known that classical reaction kinetics were founded in the field of homogeneous reactions in the gas phase; already extension to the liquid state was barricaded by various problems. Therefore, ideal kinetic conditions, i.e., working in dilute solution, were subsequently preferred.

The posters on kinetics presented on this conference deal mainly with heterogeneous kinetics, a rather complicated field. In spite of this, part of the results presented were obtained by assumption of the rate law of n th order, which is a very simple strategy.

Even before the contribution of Sharp on reaction kinetics [1], there had been many warnings and discussions on the application of such a simple concept to the evaluation of thermoanalytical records of heterogeneous reactions, of which the following is typical:

“The n th order equation has no general validity for heterogeneous solid-state reactions other than as an approximate algebraic description of the reaction.”

Similar warnings were expressed by Šesták in his interesting article on the philosophy of non-isothermal kinetics [2]. Let us reflect some of the critical arguments which were expressed.

THE ORDER CONCEPT IN HETEROGENEOUS KINETICS

The first restriction is that the concept of concentration and order of reaction should generally have no significance under such conditions. However, in many cases it is possible to discuss the fractional conversion instead. In one paper [3] an approach to the concentration concept is tried, in spite of the heterogeneous conditions, by using a diluent, lucooil M_{50} , for the reacting azodicarbonamide (used as blowing agent for polymers). By this means, the total conversion can be varied in the isothermal DSC experiments. Complimentary volumetric studies yield different data; consequently, the n th order equation is not consistent with the results, and a consecutive mechanism is postulated, the initial step being a kind of fast trimerization, followed by a slower nitrogen-evolving process.

Another argument against the use of the n th order equation is that mechanisms of heterogeneous reactions are of a completely different type than mechanisms based on mass-action kinetics [4,5]. Nevertheless, many heterogeneous processes can be described formally by the equation; moreover, there often exist geometrically founded concepts which allow the prediction of the exponent n . Thus, in another contribution [6] it is shown that the oxidation of nickel metal follows such a law, but with an exponent n of one-half. This corresponds to the diffusion model D_1 , which is not based on mass-action kinetics. In other, primarily unsuccessful cases, modifications of the n th order equation improve the agreement with experimental plots. In the paper of Flynn [7] an additive correction term is introduced into the isothermally applied equation, which stems from the initial rate observed in reactions of polymers. The reaction order may be obtained from definite ratios of the rate over the initial rate for particular times compared with precalculated values from a table.

There are some other tricks to applying the n th order concept, especially under unfavourable conditions. The most usual is to restrict the validity to a smaller portion of the total conversion. The justification, then, may resemble the argument that any curve can be represented by a straight line when the portion considered is small enough. Hence, we have not solved the problem, merely substituted it by another one, namely separation of the information into several parts which give rise to boundary problems.

Deviations from the simple order law are also discussed in the paper of Schlensky [8] on thermal decomposition kinetics of polymers. On increasing the temperature, especially for fast heating rates, the range of linearity of the logarithmic rate constant in the Arrhenius diagram is exceeded. This deviation can be described by an additional term in the exponent for the representation of the rate constant, which can be calibrated by two limit temperatures, $T(\text{infinite})$ and $T(\text{monomer})$. If the transition state theory is applicable, such a term is in agreement with an increase of the degrees of freedom at higher temperatures.

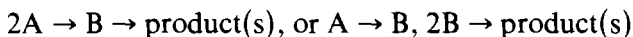
In the contribution of Flammersheim et al. [9], a reaction of great practical importance is discussed, where no simple rate law exists over the total investigation range: the cure reaction between amines and epoxies which was studied isothermally by DSC. The experimental findings, obtained by concentration series, can be described by a reaction scheme of nine steps, divisible into a noncatalytic, a catalytic and an autocatalytic part. The success in the interpretation of this example confirms the general experience that it is essential in kinetics to provide for a variation of the starting concentration of reactants or other parameters, that is to perform planned series of experiments. These may include series required for the elimination of the influence of apparatus parameters.

THE ORDER CONCEPT IN HOMOGENEOUS KINETICS—A GENERAL BASIS?

In homogeneous kinetics, reactions are mostly complex in the sense that several elementary steps in different classes of logical connection and, therefore, several temperature-dependent rate coefficients have to be discussed [10,11]. Hence, the n th order has only a true meaning for the constituting elements, i.e., the unimolecular ($n = 1$) and bimolecular ($n = 2$ only if $[A]_0 = [B]_0$) processes. My own contributions, focussed on DTA and the elimination of the physical conditions in the interpretation of the kinetics [12–14], utilize the unimolecular and/or the bimolecular rate law as a purely formalistic trial-and-error concept in order to study the differences between theoretical curves corresponding to a true one-stage model and the real curves observed. Such a strategy is promising because of the extraordinary improvement of computer techniques in recent years, especially simulation programs, allowing rapid creation of comparative material also for fundamental complex mechanisms. This is a concept for which homogeneous conditions represent an ideal training field, but which should be applicable also in heterogeneous kinetics if adequate experimental series are planned. I have made detailed suggestions [15,16].

Generally, I think that it is necessary to spend more attention on the interrelations between theory and practice, even for truly non-isothermal experiments favourably performed at linearly increased temperature. It seems that there is a general preference for isothermally controlled experiments. Information on temperature effects is then obtained by planning several experiments at different fixed temperatures. Thus, only half of the posters in my section really deal with non-isothermal kinetics. However, even measurement at increasing temperature is the main characteristic of thermoanalytical methods which distinguishes our field from the more conventional fields of kinetics. One should bear in mind that it was discussed in the TA News as to whether isothermal studies even belong to the field of thermal analysis. Such conservatism ignores the true capabilities

of thermal analysis techniques and cannot be mainly based on the inadequacies of TA equipment [10]. If any reaction occurs in a sample, there will be a local temperature change, causing a thermal gradient independent of whether the environment has been kept at a constant temperature or governed by a temperature programme. Any constraints are probably caused by the lack of applicable theoretical concepts, especially when the best mechanism is not known. Obviously our mode of thinking which was formed by recent experiences in research, or should I say is, at present, limited by conventions which originate from such experiences, this human originality initiates us to prefer the application of exact equations, wherever they may exist, in order to calculate some data which characterize the results. True non-isothermal reaction kinetics is, however, a rather more complicated field than the already “unpopular” isothermal kinetics. On the other hand, even for constant temperature no explicit algebraic expressions exist for the time-dependence of the rate of such simple reaction mechanisms as



Bessel functions have to be used here. Our mathematical language is too imperfect to offer exact, closed and explicit analytical expressions both for the calculation of curve ordinates and of important kinetic data even for simple mechanisms.

However, computer technology offers powerful alternatives, namely the generally applicable pattern recognition procedures. The sources were presented in the paper of Sharp et al. [17], but limited to isothermal measurements. These consider the fractional conversion at time t , compared to a defined fractional conversion, here one-half, for fundamental mechanisms as were summarized in the review of Šesták and Berggren [4]; this is the well-known reduced-time method, also studied by Criado et al. for non-isothermal conditions [18].

Moreover, I am convinced that my concept of the mechanistic coordinates opens a convenient and systematic way for the determination of the best mechanism in truly non-isothermal experiments [10,15,16]. These coordinates are available from peak asymmetry and peak width, the latter standardized by the apparent activation parameters of a fitted one-stage reference process. This concept is also derived from the temporary correspondence of particular conversions to fixed portions of the time or temperature axis, characterized by the reaction type index which reveals a direct analogy to the reciprocal half-time of an isothermal rate signal. This concept must be superior to pattern recognition using isothermal techniques, because it is based on the simultaneous consideration of an independent second parameter, the shape index. The significance of this quantity for the kinetic interpretation has already been mentioned by Kissinger [19], and later stated by many other groups (Juentgen, Anderson and others [20–22]).

CONCLUSION

Returning to the problem of inverse reaction kinetics discussed before, I am convinced that it is a useful and general concept to evaluate experimental kinetic plots by using the simplest procedure of all, assumption of a first-order rate law. Then, one has to look at the differences between apparent parameters obtained and those corresponding to a true first-order law. For the final interpretation, a data bank containing the fundamental heterogeneous and homogeneous mechanisms must be helpful, which can be complemented by using the same procedure for theoretical curves, available by numerical integration. Such an interpretation must never be based on a single experiment, but on series of experiments and simulations, carefully planned with respect to concentration of reactants, heating rate, mass packing density, etc. [23,24]

I hope that both the variety of established models presented at this conference, and new ideas based on pattern recognition as an established, very efficient method in informative theory, may encourage more scientists to propose additional specific reaction mechanisms. This, not the presentation of unmeaningful data, is the ultimate aim of reaction kinetics.

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