

Introduction

The term “non-isothermal kinetics” appeared in the late 1950s as a result of the extensive development of thermonalytical methods. At that time, the first commercial thermal analyzers appeared, providing sufficient precision and reproducibility of recorded data. It was also recognized that any thermoanalytical curve contains kinetic information on a process in a given temperature range. Numerous methods of estimating the Arrhenius parameters from the results of thermal analysis (TA) have been suggested [1]. However, later studies have shown that the experimental simplicity is in inverse proportion to the complexity of calculations for assessing the mechanisms of processes and determining their characteristics.

It is strongly recommended to become familiar with the work of Vyazovkin et al. [2]. This paper was developed by the Kinetics Committee of the *International Confederation for Thermal Analysis and Calorimetry* (ICTAC) as recommendations for reliable evaluation of kinetic parameters from the data obtained by means of thermal analysis methods.

Inasmuch as the TA experiment deals basically with solid samples, kinetic studies using thermoanalytical methods pertain to heterogeneous reactions. Kinetic analysis is based mainly on thermogravimetry (TG) and, to a lesser extent, on differential scanning calorimetry (DSC) data. The reasons for this are discussed below.

A formal kinetic analysis using TA data to describe heterogeneous reactions is based on certain empirical relationships, to which a physical meaning can be assigned, making allowance for certain a priori notions of the mechanism of reactions that occur in a system.

The reasoning behind the use of an empirical approach is as follows:

1. It is often rather difficult to suggest a physical and geometrical model that would correspond to the character of the process during the entire course of reaction in the temperature range under consideration. In addition, for polydisperse systems in which parallel processes occur (as in macromolecular systems with molecules of different size), modeling is a rather challenging task, so that it is better to use a physical and mathematical description of the overall process.
2. For practical purposes, a detailed study of the reaction mechanism is of less importance than the optimization of the process by determining the effect of different experimental conditions on its rate.
3. The use of empirical relationships in kinetics makes it possible to easily obtain numerical characteristics. However, without an adequate analysis of results, it is impossible to give them a strict physical meaning. A typical example is the indiscriminate use of the concepts of homogeneous reaction kinetics to describe heterogeneous reactions.

This manual focuses on the use of the Netzsch software for formal kinetic description of heterogeneous reactions based on TA data. The program package comprises the following programs: the Thermokinetics program for solving inverse and direct kinetic problems, that is for estimating Arrhenius parameters, for finding the most statistically probable type of function to describe the process under consideration, and for performing predictive calculations; the Peak Separation program for decomposing multimodal curves into separate components; and the Thermal Simulation program considering scaling effects on the basis of Thermokinetics calculation results.