A FASTER APPROACH FOR OBTAINING KINETIC PARAMETERS TEMPERATURE MODULATED THERMOGRAVIMETRY

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Kinetics is the study of the dependence of the extent or rate of a chemical reaction on time and temperature. The chief benefit of kinetics is its ability to predict performance at temperatures and times that are not easily tested.

Thermogravimetric analysis (TGA) measures mass loss versus temperature and time, providing all of the information needed to evaluate a kinetic weight loss process. Perhaps the most popular mathematical tool for evaluating kinetics of weight loss reactions is the Flynn and Wall method (1), described in ASTM standard method E1641, also used to estimate thermal endurance through ASTM standard E1877 (2). The Flynn and Wall method is a multiexperiment approach in which four or more heating rates between 1 and 10 °C/min are used to study the weight loss process. The temperature at which the weight loss occurs shifts higher as the heating rate is increased. Due to the number of slow heating rate experiments required, the Flynn and Wall approach often takes several days.

Modulated Thermogravimetry (MTGA™) enables users to obtain kinetic information in a single, time-saving experiment. A sinusoidal temperature modulation is superimposed on the underlying heating profile used in traditional TGA experiments. The result of this modulated temperature stimulus is an oscillatory response in the rate of weight loss. Deconvolution of this response, using real-time discrete Fourier transformation (DFT), leads to the desired kinetic parameters. Total decomposition often involves more than one weight loss, those often widely separated in temperature. The study of multiweight loss reactions would be lengthy with the multiple (and slow) underlying heating rates experiments used throughout the whole temperature range. Increased efficiency can be obtained by heating more rapidly between the weight loss regions. The patented Dynamic Rate Hi-Res™ TGA technology provides the ability to continuously and smoothly vary the heating rate in response to the sample's measured rate of weight loss. In temperature ranges where the weight is stable, the sample is heated rapidly. At the onset of a weight loss, the heating rate slows in response to the increasing rate of weight loss. As the reaction reaches completion, the heating rate increases again (in response to the decreasing rate of weight loss) until the next weight loss is seen.

Reaction kinetics are generally described using two equations. The first of these, known as the rate equation, describes the relationship between the rate of reaction, time, and amount of material. The second, called the Arrhenius equation, describes the relationship between reaction rate and temperature. The reaction is thought to be described when activation energy, preexponential factor, and the kinetic expression are known. Activation energy (E) is considered to be the most important of the kinetic parameters because it describes how the reaction changes as a function of temperature. These parameters are directly obtained by Modulated TGA, in a "model free" way, as it does not depend on knowledge of the kinetic function for its calculation.

In summary, modulated Thermogravimetry makes use of a sinusoidal temperature program to obtain decomposition kinetic parameters in single short experiment. The approach may be used to observe a single weight loss, or may be combined with linear or nonlinear heating (i.e., dynamic high-resolution Thermogravimetry) to scan from one weight loss region to another. Additionally, activation energy is determined without any prior knowledge of the form of the rate equation. This faster approach provides continuous kinetic information in a fraction of the time required for traditional TGA kinetic experiments.

References

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