KINETIC APPLICATIONS OF THERMAL ANALYSIS

A Comparison of Dynamic and Isothermal Methods*

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(Received September 28, 1984; in revised form January 29, 1985)

A study was undertaken to compare two computational methods of estimating kinetic parameters from thermoanlytical experiments. Examples illustrating the relationship between reaction complexity and validity of isothermal vs. non-isothermal kinetic analyses will be presented. Thermal decomposition of several compounds was studied both by isothermal and dynamic thermogravimetry (TG). For the isothermal runs, reaction order and activation energy were estimated using established methods. For the dynamic runs, the statistical method of nonlinear least squares was used to estimate all three kinetic parameters of the nth order decomposition reaction and their individual 95% confidence intervals. Both methods assumed Arrhenius temperature dependence.

There has been considerable discussion in the literature concerning the validity of kinetic data obtained by thermal analysis under non-isothermal conditions [1]. The main objections against this approach are the following:

Non-isothermal experiments imply the simultaneous change of three variables—degree of conversion, time, and temperature. This increases the error in determining reaction order and Arrhenius parameters. The error in the determination of reaction order is especially critical for condensed phase decompositions because they often exhibit fractional reaction orders. Similarly, kinetic analysis of non-isothermal data is not possible if the reaction kinetics change within the temperature range under consideration. For decomposition reactions, one often observes transitions from zero to first order at higher temperature or at higher degree of conversion. This behavior can be due to a change in the rate-limiting step in the decomposition. The non-isothermal method is also not applicable in the case of reverse parallel reactions. Apparently, occurrence of induction periods as observed in many condensed phase decompositions cannot be detected reliably [2].

Aside from these intrinsic limitations, experimental restrictions on the validity of the non-isothermal kinetics have to be considered. During non-isothermal experiments, a lag exists between the nominal temperature of the furnace and the actual sample temperature. This lag results in a temperature gradient within the sample which might seriously distort any kinetic data extracted from non-isothermal experiments.

We will show that the non-isothermal method of kinetic analysis should be preceded by specific isothermal studies to resolve the problems just discussed. Specifically, isothermal runs must be done at the upper and lower limits of the intended non-isothermal temperature range to verify that the kinetic order remains constant throughout. Additionally, these isothermal studies should reveal any reversible, parallel or autocatalytic processes that are not accounted for in the simple \( n \)th order decomposition reaction model for the non-isothermal data. After these issues have been addressed, then the non-isothermal experiments can be employed to estimate reliably the frequency factor and the activation energy. In the case of large numbers of similar samples, this approach would then result in a considerable time saving, as compared to the isothermal approach.

**Experimental**

**Materials**

All materials were research samples by American Cyanamid company.

**Procedures**

Thermogravimetric instrumentation, models TGS–1 and TGS–2 by Perkin–Elmer Corporation, was used in this study. The temperature scale of the instruments was calibrated using Curie point standards according to the manufacturer's specification. Further details have been described elsewhere [2, 3].

**Isothermal method**

Experimental details have been described elsewhere [2, 3].

**Non-isothermal method**

A FORTRAN program performs the nonlinear least squares procedure using the modified Gauss–Newton method and the Watts and Bates convergence criterion [4–8]. All computing was done on a DEC System–10 computer.