Thermochimica Acta, 59 (1982) 247–249
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

Note

GRAPHICAL ANALYSIS OF NON-ISOTHERMAL TG DATA FOR MECHANISM

LEO REICH and S.S. STIVALA

Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, NJ 07030 (U.S.A.)

(Received 7 May 1982)

Various methods have been proposed relatively recently for ascertaining mechanism in the solid state using dynamic thermogravimetry (non-isothermal TG). Thus, Criado et al. [1,2] proposed a procedure whereby a series of master curves was devised to be used with derivative thermogravimetry data. Also, the possibility of distinguishing theoretical mechanisms, using TG data, from the fraction of solid reacted at maximum reaction rate was explored. Satava and Skvara [3] also proposed the use of master curves to determine mechanism and kinetic parameters from TG data. Some workers attempted to distinguish theoretical kinetic rate laws using standard deviation, variance, or similar criteria [4–8]; others have employed double-logarithm plots [9–11]. In this paper, we will present a relatively simple graphical method for the analysis of non-isothermal TG data which can serve as a valuable adjunct to previously mentioned procedures for the determination of mechanism in the solid state.

It was previously indicated [12] that

$$g(\alpha) = (A/\mathrm{RH})\int_0^T \exp(-x)\mathrm{d}T \tag{1}$$

where, $g(\alpha) = \int_0^\alpha \mathrm{d}\alpha/f(\alpha)$; RH = constant heating rate; A = pre-exponential factor; T = temperature (K); α = degree of conversion; and, $x = E/RT$, where E = activation energy and R = gas constant.

For two TG curves obtained at different RHs, we may write from eqn. (1), for T = constant

$$\frac{(\mathrm{RH})_2}{(\mathrm{RH})_1} = \frac{g(\alpha_1)}{g(\alpha_2)} \tag{2}$$

Equation (2) was previously employed for the estimation of reaction order (n) of 'n-type' reactions in conjunction with a computer [12]. From this equation, it can be readily perceived that for a constant value of $(\mathrm{RH})_2/(\mathrm{RH})_1$, the value of n is independent of temperature and only depends on values of α_1 and α_2. Thus, values of α_1 vs. α_2 for various n values

0040-6031/82/0000–0000/$02.75

were plotted at an arbitrary constant heating rate ratio of two [12]. This method will now be extended to various proposed theoretical solid-state mechanisms.

Twelve theoretically possible kinetic functions for describing solid-state processes were utilized for plotting α_1–α_2 data for $(RH)_2/(RH)_1 = 2$. In the following are listed, in order, the function number and the corresponding expression used for $g(\alpha)$ (expressions are numbered and listed in the order they appear in the plot):

1, $[1-(1-\alpha)^{1/3}]^2$; 2, $1-(2\alpha/3)-(1-\alpha)^{2/3}$; 3, $\alpha+(1-\alpha)\ln(1-\alpha)$;

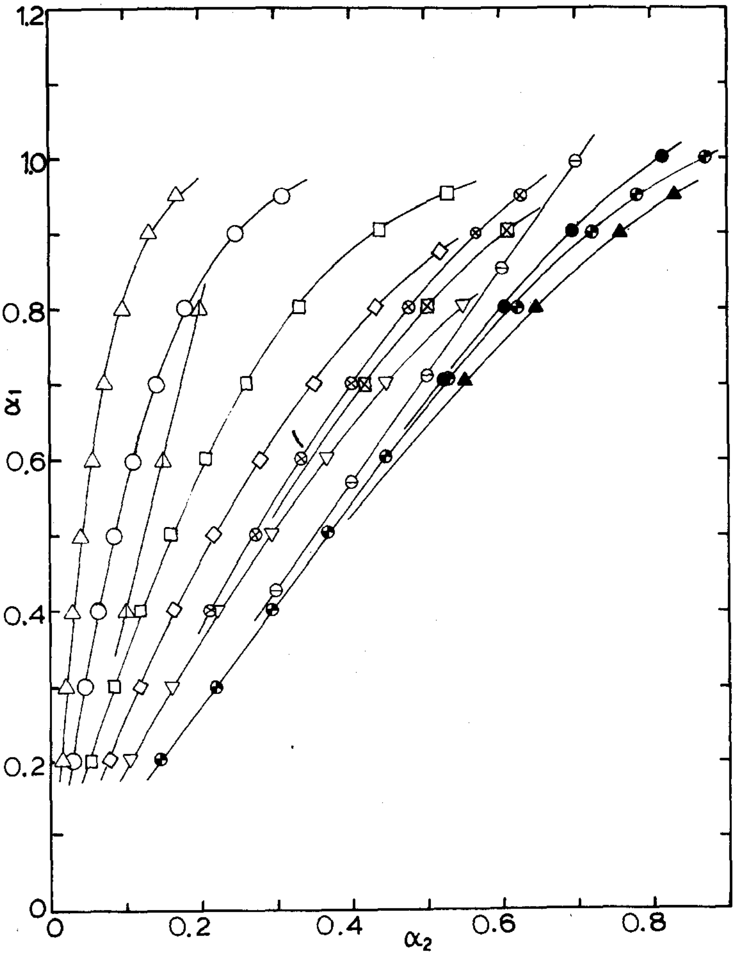

Fig. 1. Values of α_1 vs. α_2 at various TG isotherms and $(RH)_2/(RH)_1 = 2$ for 12 numbered (see text) solid-state mechanisms: ▲, 1; ⊕, 2; ●, 3; ⊖, 4; ▽, 5; ⊠, 6; ⊗, 7; ◇, 8; □, 9; ⍋, 10; ○, 11; △, 12.

$4, \alpha^2$; $5, -\ln(1-\alpha)$; $6, 1-(1-\alpha)^{1/3}$; $7, 1-(1-\alpha)^{1/2}$;

$8, [-\ln(1-\alpha)]^{2/3}$; $9, [-\ln(1-\alpha)]^{1/2}$; $10, \alpha^{1/2}$; $11, [-\ln(1-\alpha)]^{1/3}$;

$12, [-\ln(1-\alpha)]^{1/4}$

These expressions have been adequately described elsewhere (e.g. see ref. 8).

In Fig. 1 is depicted an α_1–α_2 plot $[(RH)_2/(RH)_1 = 2]$ using α-values derived from Nos. 1–12. This plot was devised so that there would be no intersections or crossings of the various curves in order to maintain clarity. From Fig. 1, it can be seen that the curves representing diffusion mechanism (Nos. 1–4) become readily distinguishable only at higher α_2 values. Similarly, the curves denoting contracting geometry mechanism (Nos. 6–7) tend to converge at low α_2 values but become more distinguishable at high α_2 values. However, curves corresponding to the Avrami–Erofeyev mechanism (Nos. 5, 8, 9, 11, 12) are quite distinct from one another at various α_2 values.

When accurate α_1, α_2, and temperature values are employed, the plot depicted in Fig. 1 (or similar ones at values of $(RH)_2/(RH)_1$ other than two) can provide corroborative support for certain solid-state mechanisms determined from non-isothermal TG data by other procedures previously described. Of course, after mechanism has been established, kinetic parameters such as E and A can be estimated.

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