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A new method for analysing non-isothermal thermoanalytical data from solid-state reactions

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Abstract

The rate equation in non-isothermal kinetics of a heterogeneous reaction involving a solid is

$$\frac{d\alpha}{dt} = Af(\alpha)\exp\left(-\frac{E}{RT}\right)$$

where α represents the fractional conversion in the solid reactant; A the Arrhenius pre-exponetial factor; T the reactant temperature; $f(\alpha)$ a so-called kinetic function that depends on the reaction mechanism; E the activation energy for the reaction, and R the gas constant. In pratice, most, if not all, non-isothermal experiments in thermal analysis are carried out at some constant heating rate $\beta = dT/dt$. In principle, the reaction kinetics may be determined (i.e. its parameters E and A measured) from several heating curves recorded at various β. Such data are often analyzed using isoconversion methods, which consider points of the same α on different curves, so that $f(\alpha)$ has identical (though unknown) magnitude and can, therefore, be 'cancelled out'. However, all existing methods rely on some approximation to the temperature integral, and are therefore subject to systematic errors.

Here, we present a new approach that needs to make no assumption about the kinetic model, involves no approximation to the temperature integral, and is easy to implement on the computer. Taking logarithms of both sides of the rate equation and then integrating with respect to α, we get

$$\int_0^\alpha \ln\left(\frac{d\alpha}{dt}\right)d\alpha = -\frac{E}{R}\int_0^\alpha \ln\frac{d\alpha}{T} + G(\alpha)$$

where $G(\alpha) \equiv \alpha \ln A + \int_0^\alpha \ln f(\alpha)d\alpha$ has the same value for isoconversion points, irrespective of β. A plot of $\int_0^\alpha \ln(d\alpha/dt)d\alpha$ against $\int_0^\alpha (1/T)d\alpha$ at a given α for a set of β's will therefore have the slope $-E/R$. © 1999 Elsevier Science B.V. All rights reserved.

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The development of non-isothermal kinetics from thermoanalytical techniques over the last 30–40 years, may, according to Flynn [1] as chairman of the Kinetics Committee under the ICTA Council, be summarised if necessary by a single statement, namely, that it was "an era in which hundreds of cute and clever mathematical manipulations were

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performed on the equation expressing the rate as a kinetic function multiplied by an Arrhenius term, and on the so-called temperature integral. This integral has no analytical solution but has been approximated by one algebraic expression or another, many of which are however gross or even inaccurate, and, used indiscrimately, serve only to create confusion and disinformation" [1]. The equation in hand is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{1}$$

where α represents the fractional conversion (increasing from 0 to 1) in the solid reactant during the course of the reaction; A the Arrhenius pre-exponetial factor, T the reactant temperature, $f(\alpha)$ a so-called kinetic function that depends on the reaction mechanism, E the activation energy for the reaction and R the gas constant. To fit this rate equation to heterogeneous reactions involving a solid under non-isothermal conditions, however, we have

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{2}$$

or

$$\ln F = \ln\left(\frac{A}{\beta R}E\right) + \ln\int_{x}^{x_0} x^{-2}\exp(-x)dx \tag{3}$$

where F is a function of α only and $x \equiv E/RT$. Unfortunately, the integral in Eq. (3) has no analytical solution in closed form. To proceed, previous authors adopt two further simplifications. First, they replace the integration limit x_0 by ∞, i.e. the initial temperature T_0 is taken to be sufficiently low so that the reaction has negligible velocity at the start of the experiment. Next, this so-called temperature integral $\int_0^{\infty} x^{-2}\exp(-x)\mathrm{d}x$ is approximated by one algebraic expression or another, many of which are, however, gross or even inaccurate, and, used indiscrimately, lead to different values of E, but serving to create confusion and disinformation [1].

We suggest instead an approach that invokes neither approximation. From Eq. (1),

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = -\frac{E}{RT} + \ln[Af(\alpha)] \tag{4}$$

or

$$\int_0^{\infty} \ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)\mathrm{d}\alpha = -\frac{E}{R}\int_0^{\alpha}\frac{\mathrm{d}\alpha}{T} + G(\alpha) \tag{5}$$

where $G(\alpha) \equiv \alpha\ln A + \int_0^{\alpha}\ln f(\alpha)\mathrm{d}\alpha$ has the same value for a given reaction under study (i.e. the same A and $f(\alpha)$) and a given α, irrespective of β. A plot of the experimental quantity on the L.H.S. of Eq. (5) against $\int_0^{\alpha}(1/T)d\alpha$, for a set of β's, will therefore have the slope $-E/R$.

With the help of contemporary thermal analyzers, all interfaced to computers, the numerical integrations of $1/T$ and $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ impose little inconvenience. Moreover, instead of integrating $1/T$ by the substitution that $T=T_0+\beta t$, we shall do so using actual readings of the temperature. This further enhances the accuracy and makes the biggest difference in differential thermal analysis, where monitored sample temperature diverges from the programmed linear rise by up to 1 K or so, and more for high β and large sample size. Indeed, our method of data analysis can deal with an arbitrary temperature program $T(t)$.

To test our approach, we apply it to the thermogravimetry of the following thermal decomposition:

$$\mathrm{SrCO_3} \rightarrow \mathrm{SrO} + \mathrm{CO_2}\uparrow$$

The strontium carbonate used was as-supplied by Fluka, of a stated purity of 4N5 and an observed particle size of 12±2 μm. A series of measurements proceeded at the nominal heating rates of 2.5, 5.0, 7.5 and 10 K/min, in a Setaram model TGA 92-16. This simultaneous TG-DTA instrument had been calibrated for temperature against the melting points of In, Sn, Pb, Zn, Al, Ag, Au and Ni, all 5N except Ni (4N), from Goodfellow; the linearity of its weight scale was confirmed by a check against a microbalance (Precisa 40SM-200A). Samples weighed from 20 to 33 mg, the heavier ones being examined at lower heating rates. Thoroughly calcined α-$\mathrm{Al_2O_3}$ (4N) from Aldrich served as the reference material, and argon, purified by molecular sieves (Type 5A, Aldrich) and flowing at 1 ml/s, as the purge gas. Gravimetric and temperature data were downloaded to a 386-PC in the form of ASCII files, to be processed by a program, written by us in Turbo C, which included a subroutine that performed numerical integration in double precision using Simpson's rule. Results in graphical

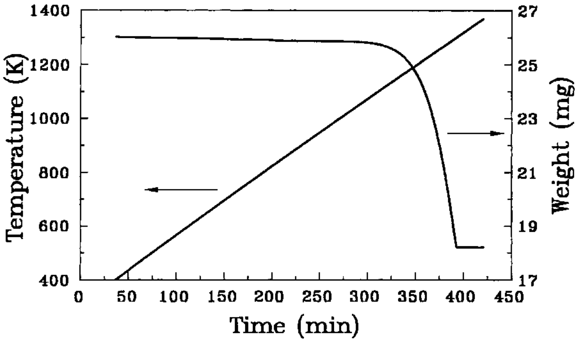

Fig. 1. Temperatures (scale on left) and weights (scale on right) of a $SrCO_3$ sample heated at β=2.5 K/min (nominal) in flowing Ar.

form, when needed, were generated by calls to SigmaPlot.

Fig. 1 presents the raw data for β=2.5 K/min nominally. Subsequently calculated 1/T and ln (dα/dt), plotted against α in Fig. 2, were integrated numerically from 0 to various α's . This procedure was then repeated for other values of β, using an identical set of α's. These integrals provide the coordinates for the points in Fig. 3. Lastly, a straight line was fitted by the least-squares method to each group of four points (with four different β's but the same α) and its slope, multiplied by -R, gave the activation energy. In this way, a number of E values were determined, pertaining to specific α's, as depicted in Fig. 4. Included there, also, are results by the older methods [2–5].

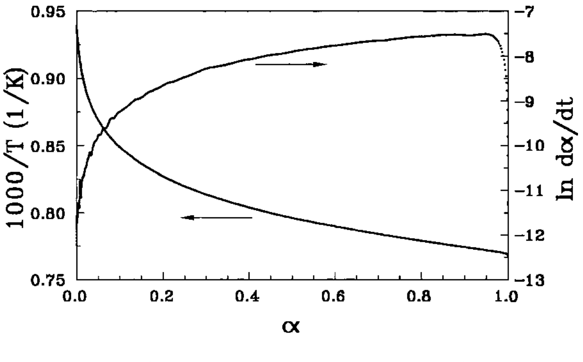

Fig. 2. Plots of 1/T and ln dα/dt (scales on left and right, respectively) vs. α.

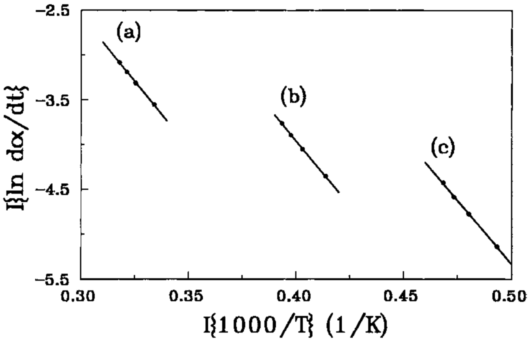

Fig. 3. I I{ln dα/dt} vs. I{1000/T}, where I{ } denotes the definite integral from 0 to α with respect to dα; a straight line is fitted to each group of four points, with different β's but all corresponding to the same α which is (a) 0.40, (b) 0.50 and (c) 0.60.

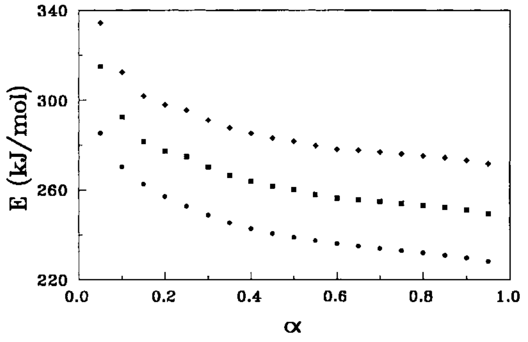

Fig. 4. Values of activation energy evaluated from the slopes of fitted lines such as those in Fig. 3 (●), from the Ozawa method (■) or from the Coats and Redfern method (◆); those derived from the Zsako and the Balarin methods are almost on top to the last ones (◆) and, therefore, omitted.

All methods, including ours, produce activation energies that deviate to greater extents in the region of small α's. This is understandable, α and ln (dα/dt) being smaller and, therefore, susceptible to larger errors near the onset of this reaction. Nevertheless, our procedure gives rise to the smallest fluctuations in E. Also, the values of E gradually, but monotonously decrease with α. However, our values come closest to those obtained in isothermal experiments [6,7], namely 230 and 222 kJ/mol. We conclude that our proposed method may be the best for analyzing non-isothermal kinetics.

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