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DYNAMIC THERMAL ANALYSIS OF SOLID-STATE REACTIONS
The ultimate method for data analysis?

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Abstract

There are many reactions of interest in which one or more of the reactants belong to some solid phases. Modern thermoanalytical instruments can conveniently provide reaction kinetic data of high precision and accuracy, from which the underlying activation energy E may be derived in principle. Unfortunately, no 'best' method yet exists for the derivation when the data have been collected with a programmed linear increase in sample temperature, unlike the case of isothermal measurements, which however suffer from experimental limitations [1]. Here we propose a method for extracting E from non-isothermal data, that promises general validity.

Keywords: non-isothermal kinetics, solid-state reactions, thermal analysis

Introduction

In the classical technique of isothermal investigations, the rate of a solid-state reaction is well described by:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\mathrm{isothermal}} = K_\infty \exp(-E/kT) f(1-\alpha) \tag{1}$$

where α represents the fraction of the solid that has reacted ($0 \le \alpha \le 1$); K_∞, the Arrhenius pre-exponential factor; k, Boltzmann's constant; T, the (constant) temperature; and f, a so-called kinetic function that depends on the reaction mechanism as well as sample geometry [2]. Under non-isothermal conditions, it can usually be assumed that the dynamic heating process is the limiting case of a succession of time intervals, during each of which the reaction advances isothermally according to Eq. (1), but at the end of which T jumps, so fast that the sample remains unchanged then. This assumption holds when the reaction under study involves no intermediate steps that are slow on the time-scale φ^{-1}, where φ denotes the chosen heating rate, so that $\mathrm{d}\alpha/\mathrm{d}t$ qualifies as a function of state and depends on α and T only. Hence the inexact differential $\mathrm{d}\alpha$ is integrable:

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{f(1-\alpha)} = \frac{K_\infty}{\Phi}\int_{T_0}^{T} \exp\left(-\frac{E}{kt}\right)\mathrm{d}T \tag{2}$$

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or

$$\ln F = \ln\left(\frac{K_\infty}{\Phi k}E\right) + \ln\int_x^{x_0} x^{-2}\exp(-x)\mathrm{d}x \qquad (3)$$

where F is a function of α only and $x \equiv E/kT$. Note the simplification from assuming that φ, the instrument controlled rate of heating, is truly constant. In principle E can then be derived from Eq. (3). Independently, $f(1-\alpha)$ is best decided from isothermal data [1, 4] amongst model forms [3].

Unfortunately the integral in Eq. (3) has no analytical solution in closed form. To proceed, previous authors adopt two further simplifications. They replace the integration limit x_0 by ∞, i.e., initial temperature T_0 is taken to be sufficiently low that the reaction has negligible velocity at the start of the experiment. Secondly,

$$\int_x^{\infty} x^{-2}\exp(-x)\mathrm{d}x$$

is approximated by some algebraic expressions and here a great variety has been offered [e.g. 5–15].

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

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t} = -E/kT + \ln[K_\infty f(1-\alpha)] \qquad (4)$$

by using α integral on both sides, then we get a more appropriate form

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

where

$$G \equiv \alpha\ln K_\infty + \int_0^\alpha \ln f(1-\alpha)\mathrm{d}\alpha \qquad (5)$$

has the same value for a given reaction under study (i.e. same K_∞ and f) and a given α, irrespective of φ. A plot of the experimental quantity on the L.H.S. of Eq. (5) *vs.* $\int_0^\alpha (1/T)\mathrm{d}\alpha$ but at a given α for a set of φ's, will therefore have the slope $-E/k$. One may then substitute the obtained value of E into Eq. (4) and determine $f(1-\alpha)$.

With the employ of contemporary thermal analysers, all interfaced to computers, the numerical integrations of $1/T$ and $\ln\mathrm{d}\alpha/\mathrm{d}t$ impose little inconvenience. Thus, instead of integrating $1/T$ by the substitution that $T = T_0 + \varphi t$, we shall do so using actual readings of the temperature. This removes the systematic error due to deviations from the assumed linear increase in temperature [16], 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 φ and large sample size. Indeed, our method of data analysis can deal with an arbitrary temperature program $T(t)$. A further comment is that, in principle, a plot of $\ln d\alpha/dt$ *vs.* $1/T$ will also produce E, according to Eq. (4) [17]. In practice, however, this introduces large errors where $d\alpha/dt$ are small, such as near the onset and sometimes near the end of the reaction. Taking their logarithm helps, but integrating ensures the greatest improvement because their contributions are then automatically reduced. The same considerations show why data analysis according to Eq. (3) by numerical integration of the temperature integral is inferior to our approach.

To test our approach, we apply it to the thermogravimetry of two types of thermal decompositions, and compare its outcomes with those derived from previous methods. The reactions studied are

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g), \text{ and}$$

$$SrCO_3(s) \rightarrow SrO(s) + CO_2(g).$$

Calcium carbonate was as-supplied by Fluka, of a stated purity of 99.5% and an observed particle size of 76±4 μm. Strontium carbonate, from Aldrich, was 99.995% pure and 12±2 μm in particle size. For each substance, a series of measurements proceeded at the nominal heating rates of 2.5, 5.0, 7.5 and 10 K min^{-1}, in a Setaram model TGA 92-16. This TG-DTA instrument had been calibrated in temperature against the melting points of In, Sn, Pb, Zn, Al, Ag, Au and Ni, all 5–9's pure except Ni, which was 4–9's, from Goodfellow, and the linearity of its weight scale had been confirmed by a check against a microbalance (Precisa 40SM-200A). Samples weighed from 20 mg to 33 mg, the heavier ones being examined at lower heating rates. Thoroughly calcined α-Al_2O_3 (4–9's) from Aldrich served as the reference material. Argon purified by molecular sieves (Type 5A, Aldrich) and flowing at 1 ml s^{-1} served as the purge gas.

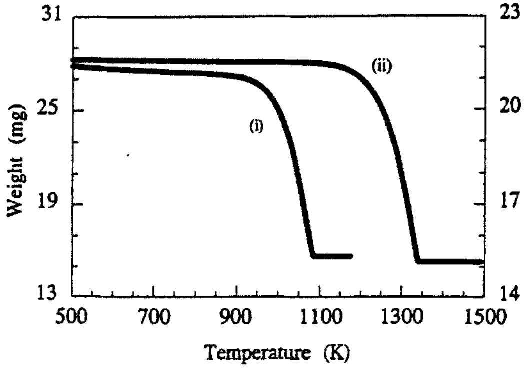

Fig. 1 Mass loss curves recorded in flowing argon at φ=5.0 K min^{-1}, for (i) $CaCO_3$ (scale on left) and (ii) $SrCO_3$ (scale on right)

Figure 1 shows two examples of raw data. For the $CaCO_3$ case with $\varphi=5.0$ K min^{-1} nominally, calculated $1/T$ and $\ln d\alpha/dt$ are plotted *vs.* α in Fig. 2. Both quantities may then be integrated numerically from 0 to various α's. This procedure is repeated for cases with other φ, using identical α's. These integrals provide the coordinates for the points in Fig. 3. A straight line is fitted by the least-squares method to each set of four points with different φ's but the same α, and its slope, multiplied by $-k$, gives the activation energy. In this way a number of E values are obtained, pertaining to specific α's, as Fig. 4 depicts. Included there also are results by older methods [5–8]. Every method, inlcuding ours, gives values that deviate to greater extents in the region of small α's. This is understandable, α and $\ln d\alpha/dt$ being small and therefore susceptible to larger errors near the onset of a reaction. Nevertheless, our method gives rise to the smallest fluctuations in E. Moreover, for any particular α, its least-squares fit (e.g. Fig. 3) achieves the highest, or in fewer instances the second highest, correlation coefficient, compared to those for other methods. Then, among its own, the coefficients for mid-range α's are closest

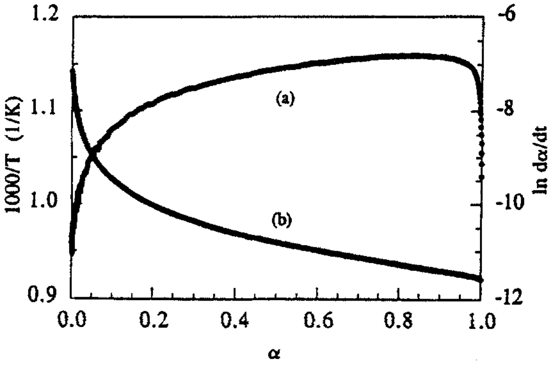

Fig. 2 Plots of (a) $1/T$ and (b) $\ln d\alpha/dt$ (scale on left and right, respectively) *vs.* α, as calculated from the $CaCO_3$ curve in Fig. 1

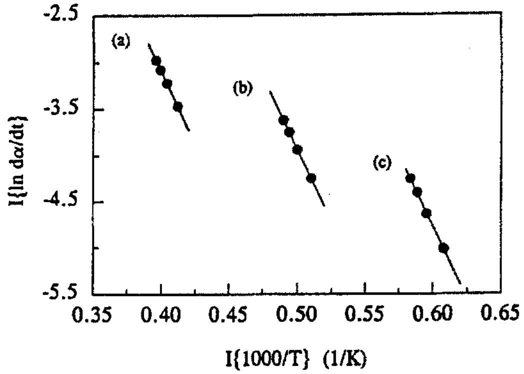

Fig. 3 $I\{\ln d\alpha/dt\}$ *vs.* $I\{1000/T\}$, where $I\{\}$ denotes the definite integral from 0 to α with respect to $d\alpha$; a straight line is fitted to each set of four points, with different φ's, but all corresponding to the same α which is (a) $\alpha=0.40$, (b) $\alpha=0.50$ and (c) $\alpha=0.60$

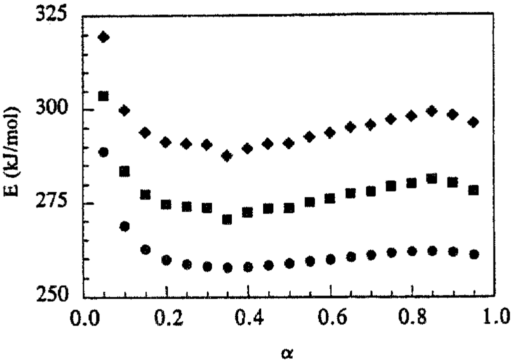

Fig. 4 Values of activation energy evaluated from the slopes of fitted lines such as those in Fig. 3 (●), from the Ozawa method (■) or from the Coats and Redfern method (◆); those derived from the Zsakó and the Balarin methods are almost on top to the last ones (◆) and therefore omitted

to unity. Since a variation in E with T or α signifies some change in mechanism [18] or parallel competitive reactions [19], its power to distinguish E over difference regimes of α and, equivalently, T, is an advantage. However, in the present situation the observed variance lacks substance in magnitude and range to claim real significance.

There is a remarkable spread in previously reported values of E for the thermal decomposition of $CaCO_3$, but under the condition of zero ambient partial pressure of CO_2, $E=250$ kJ mol^{-1} [20] which agrees with ours. The activation energy for the case of $SrCO_3$ has been put at 222 or 230 kJ mol^{-1} [21, 22]. Treatment of our experimental data with the help of the method presented here gives $E=226$ kJ mol^{-1} at $\alpha=0.50$, whilst Ozawa's approach leads to 244 kJ mol^{-1}, and those of Coats and Redfern, Zsakó and Balarin, all to 266±1 kJ mol^{-1}. The correlation coefficients in their Arrhenius plots exhibit similar tends to those described in the last paragraph. We conclude that the proposed method may be the best for analysing non-isothermal kinetics.

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