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Isoconversion method for kinetic analysis of solid-state reactions from dynamic thermoanalytical data

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The activation energy for a heterogeneous reaction involving a solid may be obtained from a plot of $\int_0^\alpha \ln(\mathrm{d}\alpha/\mathrm{d}t)\,\mathrm{d}\alpha$ against $\int_0^\alpha (1/T)\,\mathrm{d}\alpha$, where α represents the fractional conversion of the solid reactant, and $T(t)$ is the (time-dependent) reactant temperature. This new approach to the analysis of dynamic thermoanalytical kinetic data has distinct advantages over existing methods, as it needs to make no assumption about the kinetic model, involves no approximation to the temperature integral, and is easy to implement on the computer.

1. Introduction

The development of non-isothermal kinetics in thermal analysis 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 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 fractional conversion (increasing from 0 to 1) in the solid reactant during the course of the reaction; A, Arrhenius pre-exponetial factor; T, reactant temperature; $f(\alpha)$, a so-called kinetic function that depends on the reaction mechanism; E, activation energy for the reaction and R, the gas constant. This rate equation holds for heterogeneous reactions involving a solid under both isothermal and non-isothermal conditions. However, its application brings complications only in the non-isothermal situation [2, 3], which is therefore our sole concern in this paper.

In the laboratory, most if not all non-isothermal experiments in thermal analysis are "dynamic," i.e., carried out at some constant heating rate $\beta = \mathrm{d}T/\mathrm{d}t$. In principle, the reaction kinetics may be determined (i.e., its parameters E and A measured) either from a single experimental α-t curve or from several curves recorded at various β. In the former case, the single set of thermoanalytical data must first be fitted by an assumed kinetic function [4]. Without a priori knowledge of $f(\alpha)$, a "trial-and-error" procedure may be adopted [5], but its accuracy is doubtful as the "best fitting" kinetic model seldom turns out to be unique [6]. In the latter case of multiple heating rates, isoconversion methods enjoy popular use. These methods consider points of the same α on different heating curves, so that $f(\alpha)$ has identical (though unknown) magnitude and can therefore be "cancelled out."

In this paper, the applicability of several well-known isoconversional methods is discussed first. Next we present a new approach, which is then tested on the analyses of two examples of thermal decomposition. Its superiority is demonstrated experimentally.

2. Theory

It is straight forward to modify Equation 1 to read:

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = \ln[Af(\alpha)] - \frac{E}{RT}. \tag{2}$$

A plot of $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ against $1/T$ for isoconversion points on various heating curves (of different β) yields therefore E, since its slope should be $-E/R$. This method, first proposed by Friedman [7], is the most general among all methods using derivatives but, like all such methods, suffer from inherent errors arising from $\mathrm{d}\alpha/\mathrm{d}t$ values [2]. These derivatives may be measured directly off DSC or DTA thermograms, which are more noisy and for which the baselines are less well defined than in the case of TGA, or derived from TGA thermograms, via numerical differentiation, which operation however decreases the signal-to-noise ratio. The noise is particularly serious in the beginning and even more so towards the end of the reaction, when α changes slowly.

It has been claimed [8] that approximating TGA curves by power series give α derivatives of higher quality, but in fact curve fitting by polynomials or better still by cubic splines [9], however "cleverly" done, cannot reduce the random errors generated by the mathematical operation of differentiation.

Alternatively, on the assumption that the reaction under study involves no processes that are slow on the experimental time scale [2], Equation 1 may be rendered into the integral form:

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \int_{T_0}^T A \exp\left(-\frac{E}{RT}\right) \mathrm{d}t, \qquad (3)$$

where T_0 denotes the initial temperture at which the DSC or TGA measurement has started. With the further assumptions that A is not a function of T and $\mathrm{d}\alpha/\mathrm{d}t = 0$ at $T \leq T_0$, as are usually the case, and that β is truly constant throughout the measurement, then, in the notation $x \equiv E/RT$, Equation 3 may be simplified to

$$\frac{\beta}{A} \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = -\frac{E}{R} \int_\infty^x x^{-2} \exp(-x)\, \mathrm{d}x, \qquad (4)$$

or

$$\beta \frac{R}{AE} \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \int_x^\infty x^{-2} \exp(-x)\, \mathrm{d}x. \qquad (5)$$

The right-hand side of the last equation is the famous "temperature integral" $p(x)$. Since $p(x)$ has no analytical solution in closed form, lots of fun have been had in devising its algebraic expressions.

The Ozawa-Flynn-Wall or "OFW" method [10–13] adopts the approximation

$$\log p(x) \cong -2.315 - 0.4567x \quad (20 < x < 60), \quad (6)$$

so that, numerically,

$$\ln \beta \cong -1.052 \frac{E}{R} \left(\frac{1}{T}\right) + F_{\mathrm{OFW}}(\alpha), \qquad (7)$$

where log and ln are logarithms to base 10 and base e respectively, and $F_{\mathrm{OFW}}(\alpha) \cong -5.333 - \ln\{(R/AE) \int_0^\alpha [1/f(\alpha)]\, \mathrm{d}\alpha\}$ is the intercept in the plot of $\ln \beta$ vs. $1/T$.

It is also true that

$$p(x) \cong \exp(-x)/x^2 \quad (20 < x < 50), \qquad (8)$$

so that, again numerically,

$$\ln\left(\frac{\beta}{T^2}\right) \cong -\frac{E}{R} \left(\frac{1}{T}\right) + F_{\mathrm{KAS}}(\alpha). \qquad (9)$$

where $F_{\mathrm{KAS}}(\alpha) \cong -\ln\{(E/RA) \int_0^\alpha [1/f(\alpha)]\, \mathrm{d}\alpha\}$. This (KAS) method has been suggested by Akahira and Sunose [14] and Kissinger [15].

Obviously all methods like these suffer always from systematic errors in the algebraic expressions for $p(x)$. Such errors may even turn into grave inaccuracy, when researchers (or computer software) use the methods indiscrimately, without putting back the derived magnitude of E into x to confirm that x falls within its range of validity. Hence, in a previous paper [16], we have proposed a new approach that is free of unnecessary sources of random and systematic errors. Integrating both sides of Equation 2 with respect to α, we get

$$\int_0^\alpha \ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) \mathrm{d}\alpha = -\frac{E}{R} \int_0^\alpha \frac{\mathrm{d}\alpha}{T} + G(\alpha), \qquad (10)$$

where $G(\alpha) \equiv \alpha \ln A + \int_0^\alpha \ln f(\alpha)\, \mathrm{d}\alpha$ has the same value for isoconversion points, irrespective of β. A plot of $\int_0^\alpha \ln(\mathrm{d}\alpha/\mathrm{d}t)\, \mathrm{d}\alpha$ against $\int_0^\alpha (1/T)\, \mathrm{d}\alpha$ at a given α for a set of β's, will therefore have the slope $-E/R$. Note the elimination of any approximation for $p(x)$ or for any other factor. Also, that although derivatives of α are used, taking their logarithms followed by integration reduces noises twice. Note in addition that every term in Equation 10 is dimensionless, so that the relation holds mathematically, not just numerically. Lastly, that the constancy of each β no longer need to be assumed. Indeed, the real experimental values of T as a time series can be used as input data in the integration of $1/T$ with respect to $\alpha(T)$, thus eliminating another source of errors (instrumental errors in this instance).

3. Applications

To test our approach against some well-known isoconversional methods, we apply them to the thermal analyses of the following reactions:

$$\mathrm{SrCO_3(s)} \longrightarrow \mathrm{SrO(s)} + \mathrm{CO_2(g)},$$

and

$$\mathrm{2CuO(s)} \longrightarrow \mathrm{Cu_2O(s)} + \tfrac{1}{2}\mathrm{O_2(g)}.$$

Experiments were conducted in a Setaram TGA 92-16 thermal analyser, at the nominal (programme) heating rates of 2.5, 5.0, 7.5 and 10 K/min. This simultaneous TGA and heat-flux DSC instrument had been calibrated carefully in temperature and in weight scale [16]. Alumina crucibles of 100 microliters in volume made by Setaram served as sample pans and calcined α-$\mathrm{Al_2O_3}$ (4–9's) from Aldrich, as the reference. Argon dried by molecular sieves (Type 5A, Aldrich) worked as the purge gas, and its flow rate was maintained constant at 1.00 ± 0.05 ml/s by a mass flow controller (D07-11, Beijing Jianzhong Mfg.). Measured sample temperatures (*not* programme temperatures) and gravimetric readings were downloaded to a 386 IBM-compatible PC via an RS232 interface. These files were first deciphered into ASCII format and then processed by a program, written in Borland C++, which included a subroutine that performed numerical differentiation and integration in double precision after fitting the calculated $\alpha(T)$ data with cubic splines. Results in graphical form, when needed, were generated by calls to Origin for Windows version 4.10.

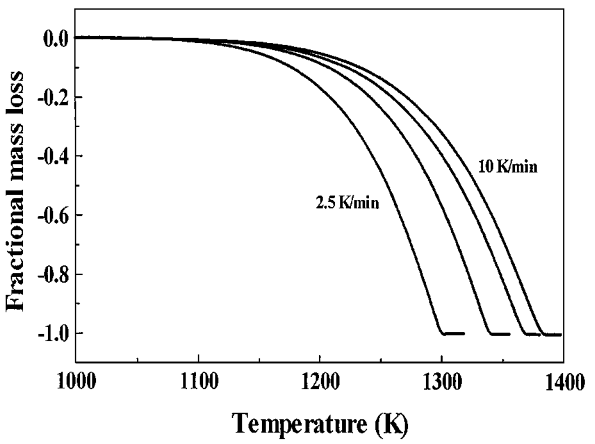

Figure 1 TGA curves, recorded at $\beta = 2.5$, 5.0, 7.5, 10 K/min, for the decomposition of $SrCO_3$.

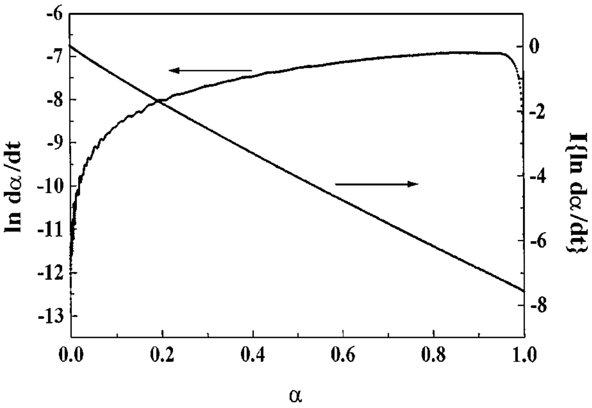

Figure 2 Plots of $\ln(d\alpha/dt)$ and its integral, calculated from the TGA data for $\beta = 7.5$ K/min in Fig. 1; I{ } denotes integration from 0 to α with respect to $d\alpha$.

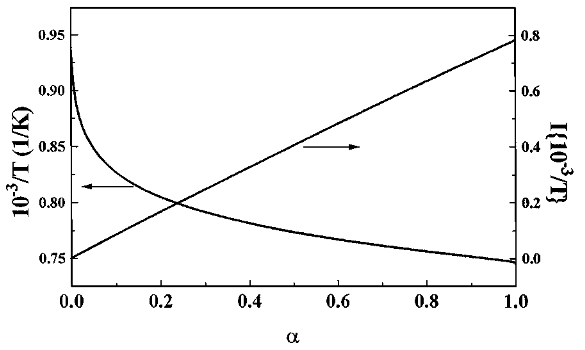

Figure 3 Plots of $1/T$ and its integral against α, for $\beta = 7.5$ K/min.

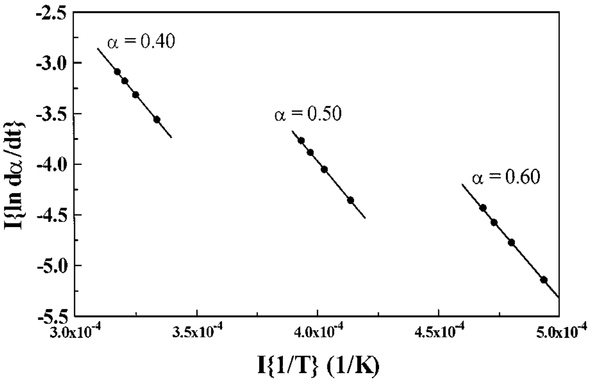

Figure 4 $\int_0^{\alpha}[\ln(d\alpha/dt)]\,d\alpha$ vs. $\int_0^{\alpha}(1/T)\,d\alpha$, a straight line is fitted to each set of four points corresponding to different β but the same α, the sets for $\alpha = 0.40$, 0.50 and 0.60 serving as examples.

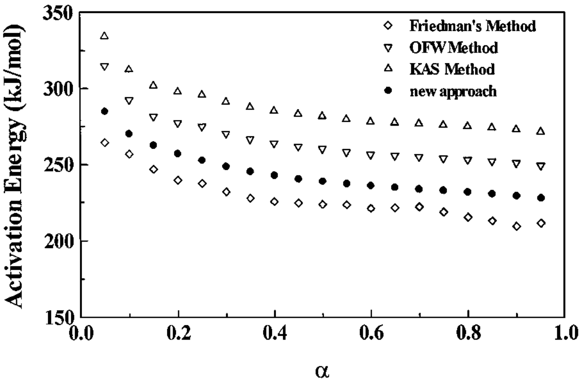

Figure 5 Activation energies of $SrCO_3$ decomposition as determined by different methods.

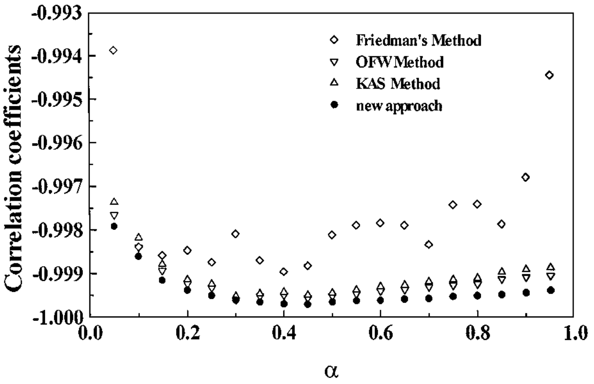

Figure 6 Correlation coefficients for $SrCO_3$ activation energy plots in different methods.

3.1. Strontium carbonate

Strontium carbonate, from Aldrich, was 99.995% pure and 12 ± 2 μm in particle size. Its TGA data for four heating rates are given in Fig. 1. Figs 2 and 3 show the evaluations of the two variable terms in Equation 10, respectively, for a heating rate. As expected, the calculated values of $\int_0^{\alpha}\ln(d\alpha/dt)\,d\alpha$ are less noisy than those for $\ln(d\alpha/dt)$, themselves already less noisy than $d\alpha/dt$ values (omitted in the figure for clarity). The calculations are repeated for other heating rates. $\int_0^{\alpha}\ln(d\alpha/dt)\,d\alpha$ is plotted against $\int_0^{\alpha}(1/T)\,d\alpha$ then: Fig. 4. The least-squares fit to each set of four points (corresponding to four different β) with the same α yields the activation energy E, equal to its slope multiplied by $-R$. In this way, the values of E at various α, from 0.05 to 0.95 in step of 0.05 can be determined (Fig. 5).

Fig. 5 also presents the activation energies that we derived by means of older isoconversion methods. The correlation coefficients among the sets of isoconversion points used in each method, old or new, are depicted in Fig. 6. Friedman's method achieves the worst corelations; our approach, the best. Both OFW and KAS methods give higher E than ours.

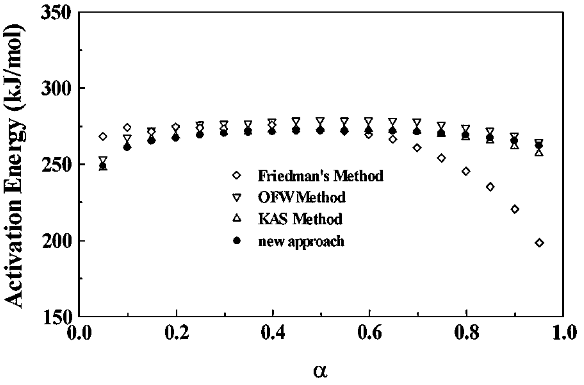

Figure 7 E for CuO from Beijing Chemical Works.

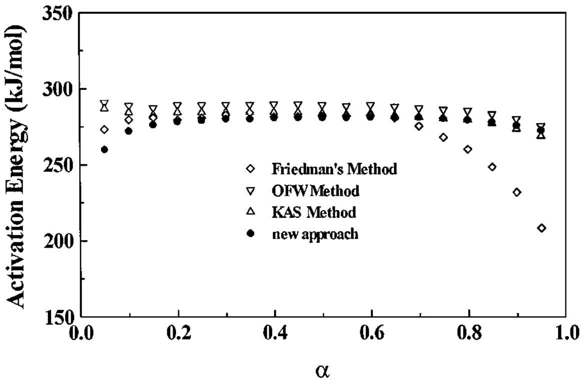

Figure 8 E for CuO from Fluka.

3.2. Cupric oxide

Two batches of reagents were examined, one supplied by Beijing Chemical Works and the other bought from Fluka, both of the stated purity 99.8%. From the results (Figs 7 and 8) we see that outcomes are independent of samples origins, and that the OFW and the KAS methods consistently lead to higher activation energies. Again, our approach offers the best correlations in the isoconversion plots (not shown).

4. Conclusions

The consistent over-estimation of E in the OFW and the KAS methods is a natural consequence of the truncation of higher-order terms in Equations 6 and 8. All isoconversion methods that invoke algebraic expansions of the temperature integral $p(x)$ will suffer from similar systematic errors. On the other hand, methods that make simple use of α derivatives, like Friedman's, will suffer from excessive random errors.

Our approach (Equation 10) avoids these pitfalls. Moreover, it is valid for all range of $x \propto E$. Its superiority has indeed been confirmed by experiments on the thermal decompositions of a carbonate and an oxide.

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