

Thermal gradients in thermal analysis experiments: Criteria to prevent inaccuracies when determining sample temperature and kinetic parameters



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ABSTRACT

Thermal analysis methods are customarily used to analyze the evolution of solid-state transformations when samples are submitted to a controlled temperature program. Thermal analysis results are generally interpreted under the assumption that no temperature gradients take place inside the sample, so that, under proper calibration the sample temperature can be determined and controlled. Two phenomena may contribute to the formation of temperature gradients within the sample: heat transport through the sample and heat evolved during an exothermic or endothermic transformation. We will provide two analytical relationships that relate the sample mass with the temperature gradient within the sample and that will provide a straightforward criterion for checking the reliability of the sample temperature. We will show that, because of their very low thermal conductivity, significant thermal gradients may occur in those samples in the form of powders. Besides, in the case of exothermic reactions and for typical experimental conditions, the heat released by the reaction significantly affects the determination of the sample temperature. Finally, we analyze how sample overheating affects the observed reaction kinetics.

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1. Introduction

Thermal analysis techniques, such as differential scanning calorimetry (DSC) and thermogravimetry (TG), are routinely used to analyze the evolution of solid-state transformations. Thermal analysis instruments are designed to monitor a given temperature dependent property as a function of time or temperature when a sample is submitted to a controlled temperature program, usually a constant temperature (isothermal) or a constant temperature rise (constant heating rate). In these apparatus, the sample temperature sensor does not have perfect thermal contact with the sample, i.e., samples are placed inside a crucible which, in turn, is placed over a sample holder which is in thermal contact with the temperature sensor. Moreover, in general the temperature program is controlled by measuring the temperature in the furnace. Under proper calibration, a reference temperature is determined from the furnace temperature which ideally would correspond to the sample temperature provided that there is no temperature delay between the sample and its holder.

Although isothermal experiments may be easier to interpret [1], constant heating rate measurements are preferred [2] because they not only allow for a larger temperature range to be analyzed, but they are faster, and they avoid the problem of non-zero initial degree of transformation [3]. However, in constant heating rate measurements, the separation between the sample and the temperature sensors results in noticeable deviations in the sample and reference temperatures from the programmed temperature [4–9]. Deviations of the reference temperature with the heating rate are approximately proportional to an apparatus characteristic time called “tau lag” [10–12]. Most calibration procedures allow a tau lag correction, so that, commercial apparatus are able to deliver an accurate and almost heating rate-independent reference temperature.

In addition, there is also a temperature delay for the sample temperature called “sample thermal lag”, which depends on sample and crucible properties and results in the formation of temperature gradients within the material, meaning it cannot be systematically corrected with an apparatus calibration.

Two different effects contribute to deviations of the actual sample temperature with the sample temperature determined from the sample holder or furnace sensor [9,13,14]: the thermal gradients related to heat transport through the sample [4,15–18] and heat evolved due to endothermic or exothermic reactions of the

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sample. Temperature gradients are known to increase with heating rate and sample mass. Excessive sample masses may result in a sample temperature shift to higher temperatures [19]. As a rule of thumb, for DSC a mass of around 1 mg is recommended, while for TG masses between 1 to 10 mg are commonly used. In fact, to confirm that sample temperature is sufficiently accurate, a check of its independence on the sample mass has been proposed [3,20], i.e., the sample mass needs to be reduced until no dependence of the evolution of the transformation on the sample mass is observed.

As for the second cause, heat evolved during transformation may result in noticeable deviations of the sample's temperature due to either self-heating or self-cooling as the reaction develops [14,20–22]. These deviations are more noticeable for larger sample masses and high enthalpy transformations [23]. As a rule of thumb, it has been proposed that the rate of heat generation must not exceed 8 mW [4].

The effect of heat transfer within the sample has been thoroughly analyzed and modeled [12,18,24,25]. The thermal inertia of the sample is responsible for a temperature delay between the sample and the sample temperature sensor, as well as a thermal gradient occurring within the sample. However, no analytical relationship between the temperature difference within the sample and the sample mass has been reported. In addition, few works are devoted to analyzing the effect of the heat evolved. Neft et al. [20], have developed a numerical model that accounts for heat and gas transport within the sample. This model is successfully applied to the analysis of soot oxidation. Merzhanov et al. [2] shows that non-isothermal kinetic methods can fail in the case of exothermic reactions. Finally, Holba et al. [18] analyze the temperature profile in a sample that exhibits a first order-phase transition. However, as far as we know, a general description of the effect of the heat evolved during exothermic reactions on the measurement is still lacking.

In this paper we numerically and experimentally analyze the artifacts induced by heat transport and the heat released by exothermic reactions. In Section 2 we provide the experiment details. In Section 3 we introduce the numerical model used in the simulations. In Section 4 we analyze the effect of the heat transport through the sample, while in Section 5 we study the effect of the heat released during the transformation. Finally, in Section 6 we analyze the effect of local overheating on the kinetic analysis of the reaction.

2. Experimental

The synthesis of barium trifluoroacetate $\text{Ba}(\text{CF}_3\text{COO})_2$ ($\text{Ba}(\text{TFA})_2$) and yttrium trifluoroacetate $\text{Y}(\text{CF}_3\text{COO})_3$ ($\text{Y}(\text{TFA})_3$) powders is described in refs. [26] and [27]. The preparation of $\text{Ba}(\text{TFA})_2$ and $\text{Y}(\text{TFA})_3$ films is described in refs. [28] and [29]. TG analysis was performed with a Mettler Toledo TG model TG851e. Simultaneous TG and DTA analysis was performed with a Setaram model SETSYS Evolution 16 thermobalance. TG curves were corrected by subtracting a consecutive identical second measurement and by measuring the final sample mass at room temperature. Powders were placed inside alumina crucibles. To facilitate gas exchange between the sample and the furnace atmosphere crucible lids were not used. Gas flow was controlled by mass flow meters. High purity gases at a flow rate of around 50 ml/min were used to control the furnace atmosphere. Water-saturated gases were obtained by bubbling the carrier gas in water at standard temperature and pressure (25 °C, 1 atm). DSC analysis was performed with a Mettler Toledo DSC model 822. Powders were placed inside aluminum crucibles and perforated lids were used to facilitate the gas exchange.

Table 1
Physical parameters of the two metalorganic powders analyzed.

	$\text{Ba}(\text{TFA})_2$	$\text{Y}(\text{TFA})_3$
Thermal conductivity, λ , W/(m K)	0.08	0.06
Specific heat capacity, c , J/(kg K)	2230	875
Density, ρ , kg/m ³	1463	1114
Thermal diffusivity, m ² /s	2.45×10^{-8}	6.15×10^{-8}
Specific heat of reaction, q , J/kg	1.0×10^6	2.75×10^5
Activation energy, E_A , J/mol	1.77×10^5	1.70×10^5
Pre-exponential constant, A , s ⁻¹	4.5×10^{13}	3.4×10^{13}
Dimensionless η	47.5	65.0

The parameters used to simulate the thermal evolution of $\text{Y}(\text{TFA})_3$ and $\text{Ba}(\text{TFA})_2$ were determined experimentally and are summarized in Table 1. Density is determined from the sample weight when it is placed in a container with well-known volume. Heat capacity, thermal conductivity and the heat of the reaction were measured by DSC. The heat of the reaction is given in refs. [26,27], heat capacity was measured at 150 °C using the method described in [30] and thermal conductivity was determined at the indium melting point (156 °C) by adapting the method described in ref. [31] to powders. Finally, determining the activation energy and pre-exponential constant is described in detail in Section 6.

3. Numerical model

Our numerical model is based on the heat conduction through the sample and crucible. Thermal losses by radiation or convection are neglected. We assume that the sample holder acts as a heat sink whose temperature is fully controlled by the temperature program and we neglect any contact resistance between the holder and the crucible. In general, crucibles are hollow cylinders, therefore, due to their symmetry (see Fig. 1), the temperature evolution may be described by a two-dimensional (2D) model [2,20,32].

$$\rho c \frac{\partial T}{\partial t} = \lambda \left(\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} \right) + \rho q \frac{\partial \alpha}{\partial t}, \quad (1)$$

where ρ is the density, c is the specific heat capacity, T is the temperature, t is the time, λ is the thermal conductivity, r and z are the radial and axial coordinates (see Fig. 1), q is the specific heat of reaction (positive for exothermic reactions) and $\alpha(r, z, t)$ is the degree of transformation ($\alpha = 0$ untransformed, $\alpha = 1$ totally transformed). We also assume that the reaction kinetics is governed by a single mechanism (single-step reaction [33]) and that it is

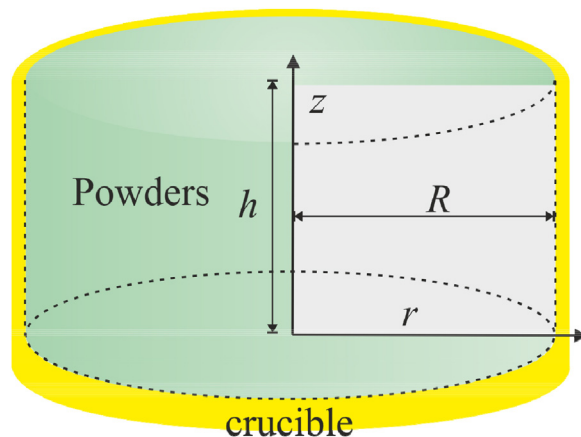


Fig. 1. Schematic representation of the geometry analyzed, Eq. (1).

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