



A general approach for temperature modulated thermogravimetry: Extension to non-periodical and event-controlled modulation



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This paper is dedicated to my shortly retired colleague Rudolf Riesen to thank for 15 years fruitful cooperation.

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ABSTRACT

Sinusoidal temperature modulated thermogravimetric analysis (TMTGA) has been proposed to get kinetic data on reactions that were investigated by TGA 45 years ago by Flynn and later by Blaine and Hahn. Because of general uncertainties of this technique, we developed a generalized approach for TMTGA using any modulation function, i.e., periodic as well as non-periodic. As a consequence of an error discussion of a TMDSC experiment, we present a new concept of the event controlled modulation function.

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1. Introduction

Temperature modulated thermogravimetry (TMTGA) was introduced in 1969 by Flynn [1]. He proposed the use of a sinusoidal temperature program to derive kinetic data from thermogravimetric measurements. Based on the isoconversional principle, he derived the average apparent activation energy of a thermal event, E , in the temperature interval of the modulation amplitude, T_a , to:

$$\frac{E_\alpha}{R} = \frac{\ln \left(\frac{\dot{\alpha}(T_1)}{\dot{\alpha}(T_2)} \right)}{T_2^{-1} - T_1^{-1}} \quad (1)$$

where E_α is the average apparent activation energy between the conversion α at the temperatures T_1 and T_2 . $\dot{\alpha}(T_i)$ is the reaction rate at T_i . Temperatures T_1 and T_2 are the maximum and the minimum of the temperature modulation. \bar{T} is the average temperature. It follows $T_1 = \bar{T} + T_a$ and $T_2 = \bar{T} - T_a$.

About 30 years later Blaine and Hahn [2] have reactivated this idea inspired by the conventional temperature modulated DSC (TMDSC) [3]. These authors have used a sinusoidal temperature modulation function superimposed by a linear underlying temperature program. The given equation for the determination

of the apparent activation energy reads:

$$E_\alpha = \frac{\ln \left(\frac{\dot{\alpha}(T_1)}{\dot{\alpha}(T_2)} \right) R (\bar{T}^2 - T_a^2)}{2T_a} \quad (2)$$

This equation follows from Eq. (1) by simple arithmetic rearrangements. This means, that Blaine and Hahn consider measurements which are performed in such a way that the underlying heating during a period of modulation can be neglected and the modulation amplitude is so small that the measured signal can be described by linear response theory. This approach is later also mentioned by Reading [4].

A dedicated discussion of the sinusoidal modulation was published by Mamleev, Bourbigot and co-workers [5–8]. These authors have proposed different procedures for determination of the apparent activation energy. Some of them should be also applicable for experiments with larger temperature amplitudes. Recently, Moukhina introduced a dedicated evaluation procedure and extensively discussed the sinusoidal modulation in the linear and the non-linear case [9].

Although the concept of the temperature modulated TGA was developed 45 years ago, the dedicated practical discussion of this technique for kinetic evaluation is relatively rare. The reason could be the relatively large error of the activation energy, especially at the beginning and the end of the reaction as it is shown in [9]. A critical discussion of the experimental conditions of the sinusoidal modulation shows deficits of this type of modulation. In this paper,

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we develop the concept of the event controlled temperature modulated TGA. This kind of modulation function has the potential for a significant improvement of the TMTGA technique.

2. Theory

2.1. Description of the measured curve

In general, we can describe the sample mass, m , during a TGA experiment by:

$$m = m_0(1 - \Delta\mu_r\alpha(T, t)) \quad (3)$$

where m_0 is the initial mass, $\alpha(T, t)$ is the conversion of the reaction as a function of temperature and time and $\Delta\mu_r = \Delta m/m_0$ is the specific mass change during the reaction of investigation. The overall mass change during the reaction is Δm . In the case that the sample mass reduces during reaction is $\Delta m < 0$ and consequently $\Delta\mu_r < 0$.

The time derivative of Eq. (3) is the DTG curve:

$$\frac{dm}{dt} = \dot{m} = m_0\Delta\mu_r\dot{\alpha}(T, t) \quad (4)$$

where $\dot{\alpha}(T, t) = dm/dt$ is the reaction rate. We assume a temperature program consisting of a low underlying heating rate, $\bar{\beta}$, superimposed by a sufficiently small temperature perturbation, $\delta T(t)$:

$$T(t) = T_0 + \bar{\beta}t + \delta T(t) = \bar{T}(t) + \delta T(t) \quad (5)$$

where T_0 is the start temperature of the measurement and $\bar{T}(t)$ is the underlying temperature. The temperature dependence of the reaction rate $\dot{\alpha}(T, t)$ in Eq. (4) can be expressed by Taylor expansion around \bar{T} . In the linear case, we neglect all higher derivatives:

$$\dot{m} = m_0\Delta\mu_r\left(\dot{\alpha}(\bar{T}, t) + \left(\frac{\partial \dot{\alpha}}{\partial T}\right)_{\bar{T}}\delta T(t)\right) \quad (6)$$

where $(\partial \dot{\alpha}/\partial T)_{\bar{T}}$ is the temperature derivative of the reaction rate at the underlying temperature \bar{T} . The temperature perturbation $\delta T(t)$ can be expressed by an arbitrary modulation function $y(t)$:

$$\delta T(t) = T_a y(t) \quad (7)$$

where T_a is the intensity (or amplitude) of the perturbation. The modulation function can be any periodical (e.g., sinusoidal, saw-tooth) or non-periodical (e.g., stochastic pulse sequences as it is used in the TOPEM technology of TMDSC [10]). In the case of a sinusoidal perturbation with the period t_p is $y(t)$ in Eq. (7) $y(t) = \sin 2\pi t/t_p$.

From Eqs. (6) and (7) follows for the total mass loss rate of the temperature modulated experiment:

$$\dot{m} = m_0\Delta\mu_r\left(\dot{\alpha}(\bar{T}, t) + \left(\frac{\partial \dot{\alpha}}{\partial T}\right)_{\bar{T}}T_a y(t)\right) = \bar{m} - \dot{m}_a y(t) \quad (8)$$

the underlying mass change rate is:

$$\bar{m} = m_0\Delta\mu_r\dot{\alpha}(\bar{T}, t) \quad (9)$$

and the intensity (or amplitude) of the modulation component of the mass loss rate is:

$$\dot{m}_a = -m_0\Delta\mu_r\left(\frac{\partial \dot{\alpha}}{\partial T}\right)_{\bar{T}}T_a \quad (10)$$

the modulated component of the mass change rate is:

$$\delta \dot{m} = m_0\Delta\mu_r\left(\frac{\partial \dot{\alpha}}{\partial T}\right)_{\bar{T}}\delta T = \dot{m}_a y(t) \quad (11)$$

Eq. (8) shows that the negative modulated component of the mass change follows directly the temperature modulation function

of the sample temperature. Eventually phase shifts or delay times between the temperature modulation and the mass change modulation are caused only by heat transfer.

The quotient of Eqs. (11) and (9) is:

$$\frac{\delta \dot{m}}{\bar{m}} = -\left(\frac{\partial \dot{\alpha}}{\partial T}\right)_{\bar{T}}\frac{\delta T}{\dot{\alpha}(\bar{T})} \quad (12)$$

If we consider only the intensity of the periodic component follows from Eqs. (10) and (9)

$$\frac{\dot{m}_a}{\bar{m}} = -\left(\frac{\partial \dot{\alpha}}{\partial T}\right)_{\bar{T}}\frac{T_a}{\dot{\alpha}(\bar{T})} \quad (13)$$

2.2. Determination of the apparent activation energy

The kinetics of a chemical reaction is often expressed by:

$$\dot{\alpha} = f(\alpha)k(T) \quad (14)$$

where $f(\alpha)$ is the temperature independent conversion function and $k(T)$ is the rate constant.

The rate constant is usually expressed by an Arrhenius equation:

$$k(T) = k_0 \exp\left(-\frac{E}{RT}\right) \quad (15)$$

here k_0 denotes the pre-exponential factor and E the apparent activation energy.

In the case of the so called model free kinetics no explicit reaction model is required. Instead, the reaction rate is described by a conversion dependent apparent activation energy $E(\alpha)$ (see e.g., [11–13]). In our scheme we determine E_{α} , the average value of E in the temperature interval between $\bar{T} - T_a$ and $\bar{T} + T_a$. Keeping in mind the temperature independence of $f(\alpha)$ (isoconversion principle) and the conversion independence of E_{α} around \bar{T} , the temperature derivative of Eq. (14) is:

$$\left(\frac{\partial \dot{\alpha}}{\partial T}\right)_{\bar{T}} = \dot{\alpha}(\bar{T})\frac{E_{\alpha}}{RT_{\bar{T}}^2} \quad (16)$$

finally we get the activation energy by inserting Eq. (16) in Eq. (13):

$$E_{\alpha} = -\frac{\dot{m}_a RT_{\bar{T}}^2}{\bar{m} T_a} \quad (17)$$

The apparent activation energy curve is mainly given by the ratio of the modulated mass loss rate intensity (this is the amplitude in the case of periodic modulation functions), \dot{m}_a , and the underlying mass loss rate, \bar{m} . Hereby, no restriction regarding the applied modulation function (Eq. (7)) has to be made. A similar equation has also been derived for a sinusoidal modulation function by Mamleev and Bourbigot [8], and recently by Moukhina [9]. They also discussed that this type of equation yields more accurate results than Eq. (2) and that for not too large temperature modulation intensities the linear approach is sufficient.

For the data evaluation it can be advantageous to analyze the course of the modulation function and not only the intensities. The larger number of data open the way for more suitable evaluation procedures. For this case we can generalize Eq. (17) using Eq. (12):

$$E(\alpha(t)) = -\frac{\delta \dot{m}(t) RT_{\bar{T}}^2}{\delta T(t) \bar{m}} \quad (18)$$

After a short discussion of the sinusoidal modulation we will introduce two different non-periodic modulation types. These are the stochastic and the event controlled modulation function.

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