



Exact analytical solution for the Kissinger equation: Determination of the peak temperature and general properties of thermally activated transformations



J. Farjas*, P. Roura

GRMT, Department of Physics, University of Girona, Campus Montilivi, Edif. PII, E17071 Girona, Catalonia, Spain

ARTICLE INFO

Article history:

Received 5 August 2014

Received in revised form 25 October 2014

Accepted 28 October 2014

Available online 31 October 2014

Keywords:

Kissinger equation

Kinetics

Peak temperature

Non-isothermal

Lambert function

Thermally activated transformation

Constant heating rate

ABSTRACT

A key parameter of many transformations when heated at a constant rate is the peak temperature, i.e., the temperature at which the transformation rate is at its maximum. The most universal approach to determine the peak temperature for thermally activated transformations is the Kissinger equation. In this paper, we solve Kissinger equation to deduce the exact dependence of the peak temperature on the heating rate. This analytical solution is based on the Lambert W -function. In addition, an approximate solution is derived that is used to infer general properties of thermally activated processes and to obtain a test to check the validity of Kissinger method.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In thermally activated and homogeneous transformations, the rate of change of a substance can be described as a function of the temperature and its state, and that the system state is a function of a single parameter: the degree of transformation, α ($0 < \alpha < 1$). Under this assumption, and supposing that the transformation is ruled by a single mechanism, the transformation rate is described by a differential equation where the contribution of the temperature and α may be factorized [1,2]:

$$\frac{d\alpha}{dt} = f(\alpha)k(T) \quad (1)$$

where t is time, T is the temperature, $k(T)$ is the rate constant and $f(\alpha)$ is the conversion function for the particular transformation mechanism. Besides, in many thermally activated solid state transformations, $k(T)$ is described by the Arrhenius dependence [3–6]:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where A is the pre-exponential term, E is the activation energy and R is the universal gas constant. When the temperature is raised at a constant rate, $\beta \equiv dT/dt$, Eq. (1) still holds, provided that the transformation rate does not depend on the thermal history. Thus, under continuous heating conditions, the explicit dependence on time of Eq. (1) can be eliminated:

$$\frac{d\alpha}{dT} = \frac{1}{\beta} k(T) \cdot f(\alpha) \quad (3)$$

From Eq. (3) one can easily derive the Kissinger equation [7] (see Appendix A) that relates the peak temperature, T_M , with the kinetic parameters and heating rate:

$$\ln\left(\frac{\beta}{T_M^2}\right) = -\frac{E}{RT_M} + \ln\left(-\frac{AR}{E} f'(\alpha_M)\right) \quad (4)$$

where $f'(\alpha_M) \equiv df/d\alpha|_{\alpha=\alpha_M}$ and α_M is the degree of transformation at T_M .

Eq. (4) has been used to determine the activation energy for a large variety of transformations [8–15]. Kissinger method relies on the determination of the peak temperature $T_{M,i}$ from experiments

* Corresponding author. Tel.: +34 972418490; fax: +34 972418098.

E-mail address: jordi.farjas@udg.es (J. Farjas).

carried at different heating rates β_i . The activation energy is obtained from a linear fit of the plot $\ln(\beta_i/T_{M,i}^2)$ versus $1/T_{M,i}$. Although Eq. (4) is exact, the Kissinger method is approximate because it assumes that the second term of the right hand side does not depend on the heating rate, β . Kissinger originally derived his equation for a first-order reaction, in this case $f(\alpha_M) = -1$ and its kinetic method is exact. For most kinetic models $f(\alpha_M)$ is approximately constant provided that E/R_{TM} is large enough [15–20] (see Appendix A). In Refs. [16–18,21,22] the values of α_M and $f(\alpha_M)$ are given, and for many reaction models $f(\alpha_M) \approx -1$. For most kinetic models, the percent error in the calculation of the activation energy is below 2% if $E/R_{TM} > 10$ [23] (a review of the literature reveals that, for most transformations, $E/R_{TM} > 10$ [24]). Typically the activation energy is around 1.5 eV (145 kJ/mol); thus, for peak temperatures around 600 K, $E/R_{TM} \sim 30$, and for $T_M \sim 1700$ K, $E/R_{TM} \sim 10$. For smaller values of E/R_{TM} other temperature dependencies may emerge due to the weak thermal activation and, therefore, Eqs. (1)–(4) must be applied with caution.

The Kissinger method has received more than four thousand citations [25]. The reason for this success are the simplicity of the model, its relative independence of the reaction mechanism [23,26] and its robustness. This is because the strong temperature dependence of the rate constant ensures a reliable determination of the activation energy from Eq. (4). The validity of Eq. (4), and therefore that of Kissinger method, is not limited by its accuracy but rather to the ability of Eqs. (1)–(3) to describe the actual kinetics. Recent papers [10,26–28] reveal that the Kissinger method is erroneously applied to systems that are not governed by Eqs. (1)–(3). The log scale involved in the Kissinger plot smoothes out the kinetic data. Consequently, linear plots are obtained even though Eqs. (1)–(3) do not describe the actual kinetics. Thus, validity of Kissinger method cannot be judged from the goodness of the linear fit. [29].

The Kissinger method fails when multiple mechanisms are involved [31–34], for heterogeneous systems [35], for transformations where the activation energy depends on α (such as structural relaxation [27,36,37]) or for transformations depending on parameters other than α and T (such as solid–gas reactions that depend on the local gas pressure [10,16,38]). To deal with these complex systems, isoconversional methods have been developed that, in addition and within the framework of the isoconversional hypothesis [39], are exact or significantly more accurate [10,11,40–43].

In general, the Kissinger method also fails for heterogeneous systems. However, in some relevant cases, such as crystallization of amorphous materials, Eqs. (1)–(3) approximately hold and it provides a reliable determination of the activation energy [8,28,44]. Since the Kissinger method assumes a constant temperature rise, it cannot be directly applied to constant cooling measurements [26,45]. Similarly, some thermally activated processes such as glass crystallization or melt crystallization do not follow an Arrhenius behavior. In these circumstances, the method may be modified [21,26,46]. In particular, it has been numerically shown that it provides reliable results [21] for a Vogel–Fulcher temperature dependence [47] but it fails in the case of melt crystallization [21,28]. Finally, thermal gradients related to heat propagation through the sample [48,49] or to the heat evolved from the sample [50,51], pose difficulties to the correct determination of the peak temperature.

As far as we know, no exact analytical solution of Eq. (4) for the peak temperature has been published. Knowledge of the peak temperature is important for both experimental and theoretical purposes. Besides having an accurate solution, it is also useful in reducing the computation time required for numerical simulations. In this paper, we solve Eq. (4) and we provide analytical solutions with sufficient accuracy for

experimental, theoretical and numerical purposes. Finally, the analytical solution is used to disclose some general properties of thermally activated processes and to develop a test to check the validity of the Kissinger method.

2. Peak temperature: solution of the Kissinger equation

Eq. (4) can be expressed in terms of the reduced activation energy $x_M \equiv E/R_{TM}$,

$$4z^2 = x_M^2 e^{x_M} \quad (5)$$

where z contains all the system parameters:

$$z \equiv \frac{1}{2} \sqrt{\frac{EAf'(\alpha_M)}{R\beta}} \quad (6)$$

Our goal is to determine x_M as a function of z : $x_M(z)$. If we take the square root of both sides of Eq. (5) we obtain,

$$z = W(z) e^{W(z)} \quad (7)$$

where $W \equiv 1/2x_M$. Eq. (7) turns out to be the definition of the transcendental Lambert W -function [52]. Lambert W -function has two branches: the principal one, W_0 , which corresponds to $W(z) > 0$, and the negative branch W_{-1} . The solution of the Kissinger equation is restricted to W_0 because $x_M \equiv E/R_{TM} > 0$. W_0 is a single-valued function that monotonically increases with z . Thus, the peak temperature is given by

$$\frac{E}{RT_M} = x_M = 2W_0(z) = 2W_0\left(\frac{1}{2} \sqrt{\frac{EAf'(\alpha_M)}{R\beta}}\right) \quad (8)$$

It is worth recalling that Eq. (8) is exact, no approximation has been used so far.

2.1. Analytical solution for experimental and theoretical purposes

There are several approximations to the Lambert W -function [53,54]. As we discussed in the introduction, $x_M > 10$ and typically x_M is around 20 or 30; the related z values are 742, 2.2×10^5 and 4.9×10^7 . Thus, we are interested in an asymptotic expansion for large values of z . In particular, the solution $W_0 = \ln(z/\ln(z) \dots)$ can be used to obtain a sequence of approximate analytical solutions [53,54],

$$W_0^{n+1} = \ln\left(\frac{z}{W_0^n}\right), W_0^0 = \ln(z) \quad (9)$$

For $x_M > 10$ ($z > 742$), the maximum relative errors of W_0^1 and W_0^2 are 5.6 and 2.1%, respectively. This error is reduced to 1.1 and 0.21% respectively for $x_M > 20$. In Ref. [24], the first term of this sequence is also proposed as a solution that takes as an initial term a value of x_M inside the interval of interest.

In Fig. 1 we have plotted the exact solution, Eq. (8), for a parameter range that corresponds to $10 < x_M < 40$. The nearly linear relationship between x_M and $\ln(z)$ is noteworthy. To take advantage of this property, we have approximated the exact solution by its first order series expansion in $\ln(z)$ around a reference peak temperature $T_{M,0}$ related to a heating rate β_0 (see Appendix B),

$$x_M = x_0 + \frac{x_0}{2 + x_0} \ln \frac{\beta_0}{\beta} \quad (10)$$

Download English Version:

<https://daneshyari.com/en/article/673087>

Download Persian Version:

<https://daneshyari.com/article/673087>

[Daneshyari.com](https://daneshyari.com)