Thermochimica Acta 540 (2012) 1–6

Contents lists available at SciVerse ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Review

Homer Kissinger and the Kissinger equation

Roger L. Blaine[a,*], Homer E. Kissinger[b]

[a] 5516 SW Willow Avenue, Corvallis, OR 97333, United States
[b] 1733 Horn Avenue, Richland, WA 99354, United States

ARTICLE INFO

Article history:
Received 20 February 2012
Received in revised form 28 March 2012
Accepted 4 April 2012
Available online 25 April 2012

Keywords:
Differential scanning calorimetry
Non-isothermal kinetics
Kissinger method
Activation energy

ABSTRACT

Homer Kissinger invented the peak displacement kinetic method that bears his name in the mid-1950s when he was an intern at the National Bureau of Standards. Because the method is rapid, easy-to-use, reliable, and uses readily available differential scanning calorimetry instrumentation, it is one of the most commonly used kinetic tools, having more than 2000 literature citations. The development of the method, Kissinger's scientific biography, advances to the approach, and practical experimental applications are reviewed.

Contents

1. Introduction 1
2. The Kissinger method 1
3. The Kissinger equation 2
4. Extension to other kinetic models 2
5. Practical aspects to the application of the Kissinger method 3
6. Limitations to the Kissinger method 3
7. Homer E. Kissinger 4
References 5

1. Introduction

During one of the meetings of the International Conference on Thermal Analysis and Calorimetry (ICTAC), the British thermal analyst Trevor Lever commented in characteristically dry British humor, "I love the ICTAC Conference. I get to put a face with an equation." I enjoyed a good laugh at the remark but it led me to thinking about the eponymous techniques that we use in thermal analysis and how they were developed. I also wondered where the authors had moved in their on-going careers. Joe Flynn and Takeo Ozawa, authors of the Ozawa–Flynn–Wall [1,2] kinetic method, and Jaroslav Sestak, author of the Sestak–Berggren method [3], regularly attend international thermal analysis meetings. But what about Hans Borchardt and Homer Kissinger, authors of the Borchardt–Daniels [4] and Kissinger [5] kinetic methods? I began a low-level quest to locate some of these scientists. Much to my surprise, through the Internet, I uncovered Homer Kissinger in retirement in Richland, Washington, where he had lived for nearly six decades. Correspondence was initiated through email and here is his story.

2. The Kissinger method

The Kissinger method is one of the most popular approaches for determining kinetic parameters by thermal analysis. The Kissinger peak displacement approach is easily applied with commonly available differential scanning calorimeters, is applicable to very small specimen sizes, and quickly and easily yields the kinetic parameters (E and Z) associated with testing for lifetime, safety, and transportation purposes [6]. Sanchez-Jimenez et al. report more than 2000 citations of the Kissinger method in the literature [7], most of them dealing with its application.

The Kissinger method is based upon a series of experiments in which small milligram quantities of the reacting material are

---

* Corresponding author. Tel.: +1 302 559 6827.
E-mail addresses: roger.l.blaine@gmail.com (R.L. Blaine), hojak@frontier.com (H.E. Kissinger).

0040-6031/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tca.2012.04.008

Fig. 1. Cato Guldberg (on the left) and Peter Waage.

heated at several heating rates (β) while the reaction exothermic peak is recorded. The exothermic peak temperature (T_m), taken to be a point of constant conversion, is measured at each heating rate. A display is prepared of $\ln[\beta/T_m^2]$ versus $1/T_m$ and a straight line is fitted to the data. The slope of the line equals $-E/R$ whereas the intercept yields $\ln[ZR/E]$ where E is the activation energy, Z is the Arrhenius pre-exponential factor and R is the gas constant (=8.314 J/mol K). A first order reaction ($n = 1$) reaction order is usually assumed.

3. The Kissinger equation

Cato Guldberg and his brother-in-law Peter Waage (see Fig. 1), first advanced the law of *massenwirkung* (mass action) in Norwegian in 1864 [8,9]. The law of mass action describes the chemical reaction equilibrium. It became more well-known some 15 years later when it was published in German, the language of science and technology [10] after publications in Dutch and French. In this much-expanded article under the original title, the concept is advanced that the rate of a reaction is described by a rate constant and is proportional to concentration of the stoichiometric reactants. Today this concept is known as the rate equation and, when applied to solid state reactions, is written in the form that the rate of reaction ($d\alpha/dt$) is proportional to some function of the amount of reactant ($f(\alpha)$)

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

where α is the fraction of reactant remaining, t is the time, $k(T)$ is the proportionality factor known as the rate constant at absolute temperature T, and $f(\alpha)$ is the "some-function-of α." The particular form or function of $f(\alpha)$ used is known as the "kinetic model."

The power of kinetic parameters lies in its ability to predict performance under difficultly reached time or temperature conditions, such as in the estimation of lifetimes. Chief among these abilities is how the reaction rate varies with temperature. A number of equations may be to describe reaction rate changes with temperature [11] but one of the earliest and most commonly used relationships was advanced by Svante Arrhenius (see Fig. 2) in 1889 and is known as the Arrhenius equation [12]:

$$k(T) = Z\exp\left[\frac{-E}{RT}\right] \tag{2}$$

The reaction rate equation and the Arrhenius equation are commonly combined into the general rate equation:

$$\frac{d\alpha}{dt} = Zf(\alpha)\exp\left[\frac{-E}{RT}\right] \tag{3}$$

Fig. 2. Svante Arrhenius.

If the general rate equation is differentiated by parts, one gets

$$\frac{d[d\alpha/dt]}{dt} = Z\exp\left[\frac{-E}{RT}\right]\frac{d[f(\alpha)]}{dt} + Zf(\alpha)\frac{d[\exp[-E/RT]]}{dt} \tag{4}$$

where β is identified as the constant heating rate dT/dt and $d[\exp[-E/RT]]/dt = E\beta/RT^2\exp[-E/RT]$. At the maximum of the reaction exothermic peak, $T = T_m$, $d[d\alpha/dt]/dt = 0$, and Eq. (4) becomes

$$0 = \frac{d[f(\alpha)]}{dt} + f(\alpha)\frac{E\beta}{RT_m^2}. \tag{5}$$

Given the identity $f'(\alpha) = d[f(\alpha)]/d\alpha$ then $d[f(\alpha)]/dt = f'd\alpha/dt$. Substituting this into Eq. (5) yields

$$0 = Z\exp\left[\frac{-E}{RT_m}\right]f'(\alpha) + \frac{E\beta}{RT_m^2}. \tag{6}$$

Solving for β/T_m^2 and taking the natural logarithm, yields:

$$\ln\left[\frac{\beta}{T_m^2}\right] = \ln\left[\frac{ZR}{E}\right] + \ln[-f'(\alpha)] - \frac{E}{RT_m}. \tag{7}$$

If the reaction is assumed to be first-order ($n = 1$) then $f'(\alpha) = (1-\alpha)$, $f' = -1$, $\ln[-f'(\alpha)] = 0$ and Eq. (7) simplifies to

$$\ln\left[\frac{\beta}{T_m^2}\right] = \ln\left[\frac{ZR}{E}\right] - \frac{E}{RT_m} \tag{8}$$

The latter is the familiar Kissinger equation.

4. Extension to other kinetic models

This clean equation form is based upon the assumption of a first-order reaction so that the term $\ln[-f'(\alpha)]$ in Eq. (7) is zero. A number of authors have extended the Kissinger method to kinetic models other than first order. For example, John Elder in his two papers (the second paper pointing out errors in the first) extended the Kissinger equation to additional nth order reactions [13,14]. A more important extension is that of Augis and Bennett [15] and the follow-on article by Boswell [16] that modified the original Kissinger method for the Avrami model to be applicable to autocatalytic reactions such as thermoset cure and crystallization.

The peak displacement method has been extended to other thermal analytical techniques through selecting an appropriate point of constant conversion on the thermal curve. In thermogravimetry, a point of constant conversion may be identified at a given conversion or it may be taken as the peak of the derivative of the mass loss profile.