



Review

Homer Kissinger and the Kissinger equation

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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.

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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

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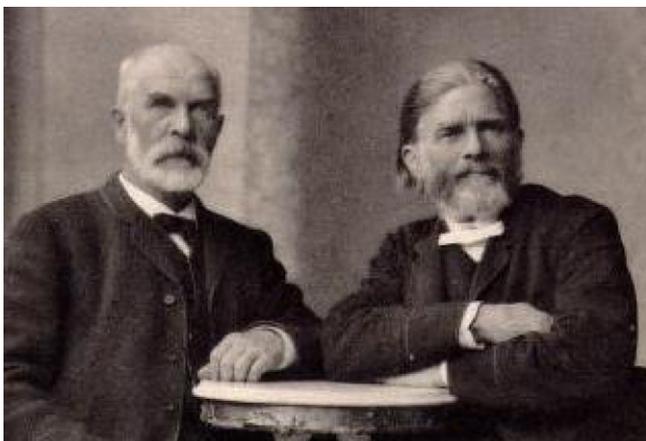


Fig. 1. Cato Guldberg (on the left) and Peter Waage.

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 ($=8.314\text{ J/mol K}$). 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 ($f(\alpha)$)

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

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]:

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

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

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



Fig. 2. Svante Arrhenius.

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

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

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

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

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

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

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

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

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

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

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 n th 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.

Akahira and Sunose chose to evaluate $f(\alpha)$ for models other than first-order [17]. Inclusion of the $f(\alpha)$ in the determination of Z is called the “extended Kissinger equation” or the “Kissinger–Akahira–Sunose” (KAS) equation and is considered to add accuracy to the method.

5. Practical aspects to the application of the Kissinger method

The original derivation of the Kissinger method was based upon differential thermal analysis (DTA) in which a temperature-sensing thermocouple was in intimate contact with the test specimen. DTA is challenged, however, by its inability to make quantitative heat flow measurements. In his seminal work, Boersma [18] observed that to perform quantitative heat flow measurements, the temperature sensor of DTA must be removed from the test specimen. As quantitative differential scanning calorimetry replaced qualitative DTA, data obtained by the variable heating rate method needed to be corrected for temperature inaccuracies created by this removal of the temperature sensor from the test specimen [19].

The first of these corrections arises from the use of heating rate as the independent variable. DSC temperature calibration is known to vary with heating rate [20]. The higher the heating rate, the greater the “lead” of the indicated temperature is over that of the test specimen. Thus many instruments need to be calibrated at each heating rate. The change in indicated temperature with heating rate ($dT/d\beta$), sometimes called “tau lag,” affects the indicated temperature. Tau lag is obtained by observing the change in indicated temperature (ΔT) as a function of a change in heating rate ($\Delta\beta$). The value $\Delta T/\Delta\beta$, which has the units of time, changes dramatically depending upon instrument design. Neuenfeld and Schick found that tau lag ranges from 43 to 0.24 s depending upon differential scanning calorimeter design [21]. For a tau lag of 43 s, a correction is required of nearly 7 K for 10 K/min heating rate.

A second temperature correction is the instrument’s thermal resistance between the temperature sensor and the test specimen. This correction, sometimes called the “leading edge slope” ($\Delta T/\Delta q$) was identified by Sestak [22] and Alan Duswalt and Jimmie McCarty as they developed ASTM International standard E698 [20]. The phase rule tells us that for a pure material melting, the temperature becomes invariant at the melting until all of the material is melted. That is, the leading edge of the observed melting endotherm should be a vertical line if the temperature indication truly represents the temperature of the test specimen. In practice, the leading edge of the melting endotherm is observed to have some slope. This is due to the temperature of the heat source continuing to rise while the melting process takes place. Thus the indicated temperature of any data point above baseline needs to be corrected for what is called the thermal resistance obtained from the leading edge of the melting curve of a pure material such as indium. This approach is commonly encountered in the calorimetric purity method [23] and other variable heating rate kinetic methods [20]. In modern differential scanning calorimeters, $\Delta T/\Delta q$ values as high as 0.36 and as low as 0.062 K/mW are observed [21].

In addition to the thermal resistance correction above, the operator needs to be aware of several other experimental concerns. One is the homogeneity of the temperature of the test specimen. During an exothermic reaction, the self-generated heat internal to the test specimen may create a temperature gradient across the test specimen leading to a range of reaction rates internal to the same specimen. To ensure temperature homogeneity, the specimen size should be chosen so that the maximum rate of heat generation is 8 mW [20] at any heating rate.

The sensitivity of the reaction is related to its energy evolved but also to the mass of the test specimen. Most workers prefer an

approximately 1 mg specimen size for kinetic work. This keeps the reaction gas volume small and reduces the total amount of energy generated – both safety measures.

A decomposition reaction is often accompanied by a loss of volatile products. These products must find their way to the surface of the particle and be exhausted. To facilitate this process, test specimens are often ground in a liquid-nitrogen, cryogenic mill to give small particle sizes with large surface area. The cold temperatures of the cryogenic mill prevent localized heating that may advance the decomposition reaction.

Reactions conducted in an open sample pan are sometimes observed to be irreproducible under similar experimental conditions. This is attributed to the irreproducible loss of reaction products. Moreover, the aluminum specimen pans commonly used in differential scanning calorimetry are thought to catalyze some decomposition reactions. Many scientists use gold or gold-plated pans or glass ampoules to avoid interaction with the test specimen. When the decomposition volatile gases are held in the vicinity of the test specimen and ambient pressure is maintained, a much higher degree of repeatability is obtained. Hermetically sealed gold pans containing a microscopic “laser-drilled” hole of 75 μm diameter produce reproducible results. This configuration is thought to retain the decomposition gases in the “headspace” over the test specimen permitting equilibrium to be established between reactants and products while allowing excess pressure to escape.

Some workers use high-pressure metal capsules such as those provided by the glass- or gold-lined Swiss Sicherheitsinstitute (Institute for the Promotion of Safety and Security) containers or glass ampoules such as those popularized by Larry Whiting et al. [24] to retain all of the evolved gases in the vicinity of the test specimen. These sealed containers work well, but are somewhat larger in mass than conventional specimen containers, and this larger mass dampens the measured energy released during the reaction, reducing sensitivity. Moreover, the internal pressure varies dependent upon the specimen mass.

Another concern deals with the number of determinations needed to obtain reliable kinetic information. In principle, the number of determinations needs only be equal to the number of parameters to be determined. For an assumed first-order reaction, then only two experiments are needed to determine activation energy (E) and pre-exponential factor (Z). In practice, even under the best of experimental condition controls, kinetic results show considerable imprecision. An interlaboratory test, using the same supplied material and the same test method, showed the between-laboratory reproducibility for the determination of kinetic parameters to be about 10% for activation energy and $\ln(\text{pre-exponential factor})$ and about 22% for the reaction order [25]. To enhance accuracy, the operator is encouraged to make replicate determinations over a large range of heating rates. For most thermoanalytical kinetic work, the lowest practical heating rate (due to sensitivity and length of experimental time) is about 0.5 K/min. Experience shows that the maximum practical heating rate is often about 10 K/min to satisfy the homogeneity requirement above. One of us (RLB) recommends duplicate determinations at each of 5–6 heating rates; 0.7, 1, 2, 4, 7 and 10 K/min. The mean values obtained from replicate determinations provide the best tool to address the imprecision in the determined kinetic parameters.

6. Limitations to the Kissinger method

Even though it is widely used, there are a number of limitations to applying the Kissinger method. Many of these are carefully discussed by the Kinetics Committee of the International Conference on Thermal Analysis and Calorimetry (ICTAC) in their overview of kinetic computations [26].

One of the common assumptions made when determining the kinetics parameters of a reaction is that the same mechanism, and thus kinetic parameters, hold throughout the reaction. Garn and others have pointed out that rarely this is the case [27]. The activation energy determined at the single point reaction peak temperature may not be the same as that observed during the early or late portions of the reactions. Alternative kinetic methods such as the variable heating rate mass loss methods [20] or modulated thermogravimetry [28] which may determine activation energy at any conversion, may be useful to observe this characteristic of changing activation energy with conversion. Nonetheless, the single-point Kissinger method provides sound kinetic parameters for the mid-conversion range of many reactions and is thus practical for most applications such as estimation of lifetime.

Another practical limitation is that the method may not be used for cooling experiments [29]. This limitation is both mathematical and practical. Vyazovkin points out that the Kissinger equation is derived only for heating experiments and is not mathematically sound for cooling [29]. Practically speaking, supercooling, common in cooling experiments, may lead to self-heating, even for very small specimens. Such self-heating may lead to an erroneous assignment of the temperature at heat flow maximum.

7. Homer E. Kissinger

Homer Kissinger, author of the variable temperature method eponymously known as the Kissinger method, was born on 29 August 1923 in Ottawa, Kansas, to Howard and Leota Kissinger. He was the oldest of three siblings, himself, one brother and one sister. His father was a partner with a brother and their father in the business of breeding and selling high-quality Guernsey dairy cattle. The business was prosperous before 1929 but rather “iffy” thereafter. As a youngster, Homer learned to read early, loved reading and read everything he could get his hands on. He attended high school from 1936 to 1940 in those troubled times before World War II; his favorite subjects were physics, mathematics, and mechanical drawing. He tried out for football, but no big sparks there.

After graduation, he entered the family business but it was a poor fit. So he went to radio school and became acquainted with commercial transmitters and receivers and emerged with an FCC license.

The United States entered World War II in December 1941 and Homer enlisted in the Army in October of the following year. He served in radio maintenance at a flight training base in Texas. In May 1943, the Army announced the Army Specialized Training Program (ASTP) to send qualified enlisted men to college. Homer took advantage of the program and was sent to Louisiana State University. Manpower shortages terminated the program in 1944 and students were used to fill out combat units overseas. Homer served with the 395th Infantry Regiment, 99th Division, in Belgium and Germany, and was discharged in 1946 with a Bronze Star, Purple Heart, and a skull full of demons.

The GI Bill saw Homer enrolled in Kansas State University (KSU). The demons could not coexist with an Introduction to Theoretical Physics and gradually faded away. Homer says, “I’d recommend this treatment for present-day veterans but I doubt that the Veterans Administration will ask me.”

In his junior year, the National Bureau of Standards (NBS), now the National Institutes of Standards and Technology (NIST), announced openings for “student aides.” Homer applied, was accepted, and spent the summer of 1948 in Washington, DC, working in the “quartz lab” whose mission was to develop better methods to produce quartz oscillators for frequency control in military devices. He returned to KSU and received his BS degree in 1949. Following graduation, Homer returned to NBS for a second

internship in the Mineral Products Division and, in the fall of 1949, Homer returned to KSU where he worked on his MS degree in the area of “X-ray Study of the Decomposition of Kaolinite,” part of a joint program by the Physics and Chemistry Departments. His work, published in *Soil Science* [30], was chosen as KSU’s Sigma Xi best paper of the year.

Returning to NBS in September 1950, he was assigned to the Electron Microscopy Laboratory under the talented Max Swerdlow. Homer remained there for several years becoming one of R.C.L. Mooney’s staff, determining crystal structures of inorganic phosphates and became a decent X-ray crystallographer in the process.

NBS had a differential thermal analysis (DTA) setup, operated primarily by Barbara Sullivan. This apparatus was very crude by today’s standards, but it had a very useful capability of precise temperature control at any chosen heating rate. Homer’s only interest then was observing the reaction progress to select sampling points for X-ray study.

A paper by Murray and White [31] appeared about this time, predicting a shift in differential thermal analysis (DTA) peak temperatures with heating rate. They used a simple kinetic equation to explain the shift in peak temperature with heating rate of an endothermic decomposition reaction. Homer explains, “It seemed obvious to me that the observed shifts could be used to determine the kinetic constants, and a little recreational mathematics showed how to do it. I immediately sat down to do the calculation in reverse, using experimental values that we had or could easily get, to determine activation energy. We tried it and it worked.”

“This work was first published in the *NBS Journal of Research* [32]. “I went to great pains to make it as reviewer-proof as I could,” Homer continued. He spent a lot of time on the manuscript, encouraged by his NBS management. The paper attracted some attention and he was invited to present a paper at an American Ceramic Society meeting, and later asked to submit a paper to *Analytical Chemistry* [5]. Homer also went to a couple of Gordon Conferences, where he met both Murray and White whom he describes as “both Britishers and gentlemen.” “I was able to express gratitude for the jumpstart that they provided. They should get the credit (for this work) and not I,” he said.

Following his two publications, Homer spent a lot of time in correspondence, some with mathematicians who insisted he was all wrong in differentiating with respect to one variable when the equation plainly contained two. Homer writes, “I pointed out again and again that by making temperature a linear function of time, there was but one variable. Some of those people just wouldn’t buy that.”

In the late 1950s, Homer was appointed to the Synthetic Mica Committee, as an alternate for the NBS member. Synthetic mica was a high-priority item for the military, which bought vacuum tubes by the millions; each tube containing a small mica sheet on which the electrodes were mounted. Much of the mica came from other countries and the few mica mines in the USA could not possibly fill the demand. So the military spent lot of money and effort, until it realized that transistors were replacing vacuum tubes almost everywhere. The program was abruptly cut. “It was fun while it lasted,” Homer joked.

In the 1950s, NBS was a great place to be. The (President) Eisenhower Administration, however, was not science-friendly, and Senator Joe McCarthy made it worse. By the end of the decade, the Kissingers were ready to move on. They had three young boys by then, “our contribution to the Baby Boom,” he wrote.

“I left NBS in 1960 for General Electric, which was the contractor for the US Atomic Energy Commission’s (now Department of the Energy) Hanford Laboratories in Richland, Washington. That was the start of 27 rewarding years (see Fig. 3). The work involved just about every aspect of X-ray crystallography with the object of learning about radiation-induced defects in metals. When Battelle



Fig. 3. Homer Kissinger circa 1970.

Memorial Institute (now Pacific Northwest Laboratories) took over the (Hanford Laboratories) contract in 1965, “the only thing we lowly workers noticed was a new name on our paychecks.”

Homer retired from Battelle in 1987 as a Senior Research Scientist when he developed hearing problems that made his professional life difficult (see Fig. 4). He reports that since that time, he has been out of touch with the world of science but remains a member of the science research honorary fraternity Sigma Xi. Homer's hearing continued to decline with time. He is now totally deaf but has a cochlear implant that gives him a little useful hearing. Everyday telephone conversation is impossible but he uses a captured telephone system in which a specially trained operator puts the caller's words on Homer's computer screen. Homer reports that it is a “pain,” but it works.

Homer married Elizabeth Jane Stinebaugh (she prefers “Jane” and hates “Betty” or “Liz”) in 1948 in her church in Princeton, Kansas. Jane grew up in a small town 7 or 8 miles from the Kissinger family home, but they did not meet before attending KSU. Their four sons were born in four different states. Homer jokes that “when

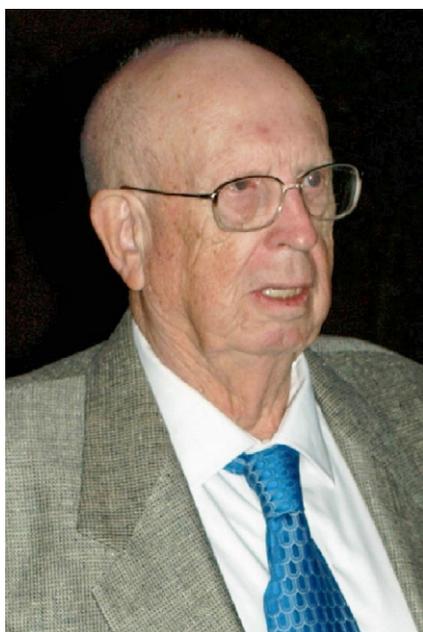


Fig. 4. Homer Kissinger circa 2010.



Fig. 5. The Kissinger family in a photograph taken in 2008. Clockwise, from left, Charles Kissinger, PhD in Biomolecular Structure, self-employed as a consultant in San Diego, California, Donald Kissinger, BS, a plant engineer at Palos Verde nuclear plant near Phoenix, Arizona, Brian Kissinger, MS in Sports Management, teacher and basketball coach in Spokane, Washington, and Alan Kissinger, BS in Business, Credit Manager and Vice President of an equipment leasing firm in Auburn, Washington. In the center are Jane and Homer Kissinger.

we stopped moving, no more kids.” A family photograph taken at Homer and Jane's 60th wedding anniversary is shown in Fig. 5 (Note added in review - Jane Kissinger died 27 March 2012).

Homer writes, “I suppose achieving eponymy is something to be proud of, but when it occurs in a field not one's own, I don't know.” A humble man, Kissinger seemed far prouder of his first publication on the decomposition of kaolinites than in the equation that carries his name. He explained, “Anyway, DTA was never my chosen field and I considered myself an X-ray crystallographer and would much rather have achieved recognition in that field. The work that I found most satisfying was done at Hanford. There was no big scientific impact, however, as the majority of the work was published in seldom-read journals of the nuclear materials field.”

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