

Note

THE EFFECT OF TEMPERATURE LAG ON ACTIVATION ENERGY DETERMINED BY NON-ISOTHERMAL ANALYSIS

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ABSTRACT

The need for accurate determination of activation energies of reactions is highlighted. An expression is derived which shows the effect of temperature lag between the sample and the thermometer on the activation energy determined by non-isothermal experiments. It is shown that the use of uncorrected temperatures makes the Kissinger plot curved, a fact in agreement with features generally observed in the literature. It has also been shown that adequate correction for the measured temperatures results in the disappearance of the curvature of the plot.

INTRODUCTION

Thermal analysis is a popular and convenient tool in studying reactions of different kinds. The requirement of only a small amount of material coupled with the comparatively fast and easy performance of experiments makes the technique attractive. Thermal analytical instruments monitor the changes in properties caused by different processes. For example, the evolution of gaseous products during decomposition leads to a loss in weight of the sample and is the parameter monitored in DTG. Evolution or absorption of heat during reactions results in a difference in temperature between the sample and the control and is the signal of interest in DTA, since this produces measurable exotherms in differential scanning calorimetry experiments. Though thermal analytical experiments can be performed isothermally, more popular is the scanning method in which the temperature is varied at a constant rate and the changes monitored as a function of the sample temperature.

Thermal analysis is of great use in studying reaction kinetics. Fundamental to kinetics studies is the rate equation

$$S = dx/dt = A(1 - x) \exp(-E/RT) \quad (1)$$

where x is the fraction of reactant transformed, A is the pre-exponential factor which is a constant, and E is the activation energy. The determination of E is one of the aims of kinetics studies [1]. Equation (1) can be used

to extrapolate the reaction rate at temperature T_2 from the rate determined at temperature T_1 , if the value of E is known:

$$S_2 = S_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \quad (2)$$

Taking logarithms and differentiating eqn. (2) to determine the uncertainty in S_2 due to the uncertainty in the experimental value of E , we get

$$dS_2/S_2 = (dE/R)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (3)$$

The values of E for crystallization of the glass $\text{Fe}_{80}\text{B}_{20}$ determined by different authors [2] show a variation of about 0.3 eV (7 kcal mol⁻¹) around the average value of 2.4 eV (55 kcal mol⁻¹) determined at temperatures around 740 K. We will now see the effect of this uncertainty on the extrapolated rate of transformation at, say, 600 K.

Substituting the above values into eqn. (3), it is seen that the calculated rate will be uncertain by more than 100%. It is therefore desirable that the activation energy should be determined with sufficient accuracy. It is shown in ref. 2 that, after applying a correction for the difference in the measured and the actual sample temperatures, the activation energy differed by about 15% from the uncorrected one. It is therefore useful to analyse the effect of experimental errors on the results obtained by methods used to determine the activation energy from non-isothermal experimental techniques. The dependence of the measured temperature on different factors is a well documented fact [3]. Among factors that influence the difference in actual and measured values of temperature, the heating rate and heat capacity of the sample are important [4]. The non-vanishing thermal resistance between the thermometer and the sample produces a temperature gradient between the two. This temperature lag can be significant at high scanning rates. Since the Kissinger method often employs data obtained at high scanning rates—this is especially true for the study of the kinetics of crystallization of metastable glassy metals—it is worth examining the effect of such systematic errors on the results obtained by this method.

This paper derives the effect of a temperature lag on the characteristics of the Kissinger plot. In the Kissinger method, $\ln(v/T_p^2)$ is plotted against $1/T_p$ to give a straight line with gradient $-E/R$, where v is the heating rate employed, T_p is the peak temperature and E is the activation energy.

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In the following analysis the subscript "p" denotes parameters corresponding to the actual values and "pm" parameters corresponding to the erroneous measured values:

$$x_p = 1/T_p \quad (4)$$

$$y_p = \ln(v/T_p^2) \quad (5)$$

From eqns. (4) and (5) we obtain

$$y_p = \ln(vx_p^2) \quad (6)$$

The activation energy is given by the slope of the y_p vs. x_p plot. The slope is given by differentiating eqn. (6),

$$dy_p/dx_p = (1/v)(dv/dx_p) + 2/x_p = -E/R \quad (7)$$

A first-order correction of the measured peak temperature T_{pm} due to the heating rate is given by

$$T_{pm} = T_p + av \quad (8)$$

where a is a constant for a particular experiment given by $a = RC$, where R is the thermal resistance of the region between the sample and the temperature measuring unit and C is the heat capacity of the sample [4]. The above terms corresponding to T_{pm} are given by

$$x_{pm} = 1/T_{pm} \quad (9)$$

$$y_{pm} = v/T_{pm}^2 \quad (10)$$

$$y_{pm} = \ln(vx_{pm}^2) \quad (11)$$

$$x_{pm} = 1/T_p(1 + av/T_p) \quad (12)$$

For small corrections of temperature, after neglecting smaller terms, eqn. (12) becomes

$$x_{pm} = x_p(1 - avx_p) \quad (13)$$

$$dx_{pm} = dx_p[1 - 2avx_p - ax_p^2(dv/dx_p)] \quad (14)$$

The slope of the plot of the measured values is obtained by using eqn. (11) as

$$m = dy_{pm}/dx_{pm} = (1/v)(dv/dx_{pm}) + 2/x_{pm} \quad (15)$$

Substituting for x_{pm} and dx_{pm} in eqn. (15) and using eqn. (13) and eqn. (14) gives

$$m = (1/v) dv/\{dx_p[1 - 2ax_p - ax_p^2(dv/dx_p)]\} + 2/[x_p(1 - avx_p)] \quad (16)$$

Again neglecting smaller terms eqn. (16) becomes

$$m = (1/v)(dv/dx_p)[1 + 2avx_p + ax_p^2(dv/dx_p)] + (2/x_p)(1 + avx_p) \quad (17)$$

Expanding eqn. (17) and substituting for dv/dx_p using eqn. (7) we get after neglecting smaller terms

$$m = (-E/R)[1 - avx_p^2(E/R)] \quad (18)$$

Again, we will estimate the approximate deviation of the measured activation energy for crystallization of the glass $\text{Fe}_{80}\text{B}_{20}$ determined in ref. 2. The value of E obtained after correction is 2.59 eV ($59.6 \text{ kcal mol}^{-1}$); the peak temperature obtained at the heating rate of 50 K min^{-1} is around 740 K. Substituting these values into eqn. (18) we get

$$m = -(E/R)(1 - 2.75a) \quad (19)$$

The value of a for the Perkin-Elmer DSC-2 as given in ref. 4 is 0.03–0.05. Substituting this value for a in eqn. (19), we see that the estimated activation energy will be uncertain by 9–14% in agreement with the correction of 15% which the authors applied for their Dupont 990 system.

DISCUSSION

Equation (18) determines the shape of the Kissinger plot. Obviously, the deviation of the slope from the value of $-E/R$ is proportional to the correction, a . A typical Kissinger plot for crystallization of metallic glass is given in Fig. 1. The instrument used is a Perkin-Elmer DSC-2. The equipment was initially calibrated using the melting point of zinc at a heating rate of 10 K min^{-1} . The crystallization thermograms were recorded at four different scan rates of 10, 20, 40 and 80 K min^{-1} . Plot (a) in Fig. 1 is obtained with the measured values of peak temperature using the instrument calibrated for the heating rate of 10 K min^{-1} . The peak temperature increases with increasing heating rate. The factor vx_p^2 increases along the

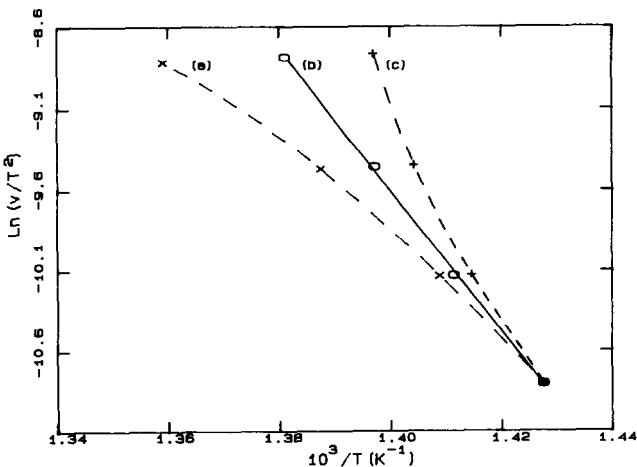


Fig. 1. Kissinger plot of the crystallization exotherm of Cu-Ti metallic glass: curve (a) obtained with measured temperatures; curve (b), obtained after adequate correction for temperature lag; curve (c), obtained after excess correction for temperature lag.

ordinate. It is evident from eqn. (18) that in going along the ordinate the magnitude of the slope decreases making the plot concave towards the origin. This is what is observed in the curved plot (a) in Fig. 1. If the curvature were actually caused by the temperature lag, a correction of the kind given by eqn. (8) with a suitable value for a would result in the disappearance of the curvature. It was found that when $a = 0.17$ the plot obtained with the corrected temperatures lies on a straight line given by plot (b) in Fig. 1. This line appears to be a tangent to the curve (a) at the point corresponding to the correct measured value of the peak temperature, in this case that obtained for the heating rate of 10 K min^{-1} . Plot (c) is obtained when $a = 0.3$, which is equivalent to applying an excess correction. As is clear from plot (c), that when the excess correction is applied the points lie on a curve convex towards the origin. Over-corrected data are equivalent to using data which require correction. Applying eqn. (8) with a negative value of a , makes the plot convex by virtue of eqn. (18).

The above results show that the curvature found in the Kissinger plots reported in the literature [2,5,6 and 7] may be attributed to inadequate correction of the measured sample temperature. Furthermore, as is clear from eqn. (18), the activation energy obtained from the uncorrected Kissinger plot is lower than the actual activation energy if a is positive, i.e. if the instrument is only calibrated for a fixed low heating rate. This result is obtained here as it is in ref. 2, where the corrected activation energy was 15% higher than the uncorrected one. The effect of experimental errors on activation energies determined from plots obtained by other methods can be analysed along similar lines to those outlined in this paper.

REFERENCES

- 1 H.E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
- 2 J.A. Leake and A.L. Greer, *J. Non-Cryst. Solids*, 38–39 (1980) 735.
- 3 G.W.H. Hohne, H.K. Gammenga, W. Eysel, E. Gmelin, and W. Hemminger, *Thermochim. Acta*, 160 (1990) 1.
- 4 S.C. Mraw, *Differential scanning calorimetry*, in C.Y. Ho (Ed.), *Specific Heat of Solids*, Vol. 1–2, Hemisphere Publishing, New York, 1968, chapter 12, p. 395.
- 5 W. Jintang, W. Shueli, D. Bingshe and Li Shuling, *Proc. 4th Int. Conf. on Rapidly Quenched Metals*, Sendai, 1981, p. 731.
- 6 K.M. Yang, Y.J. Wong, and Q. Jang, *J. Non-Cryst. Solids*, 101 (1988) 65.
- 7 K. Matusita and S. Sakka, *J. Non-Cryst. Solids*, 38–39 (1980) 741.