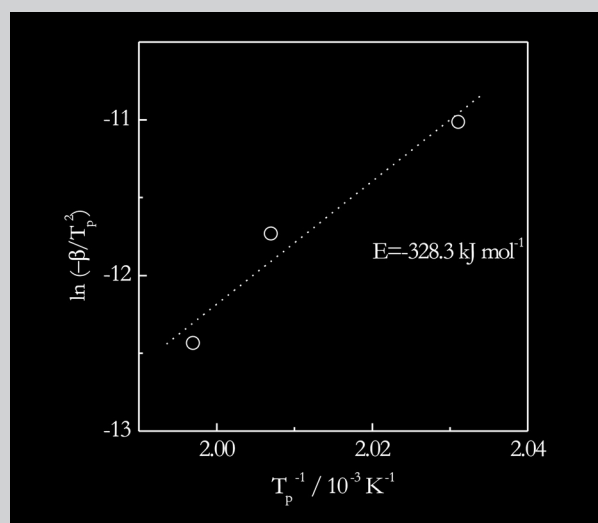


Communication: The activation energy, E , of nonisothermal crystallization of polymer melts has been frequently evaluated by the Kissinger equation with positive rates of temperature variation, β . It is demonstrated that dropping the negative sign for β is a mathematically invalid procedure that generally makes the Kissinger equation inapplicable to the processes that occur on cooling. Simulations and an experimental example demonstrate that the use of this invalid procedure may result in erroneous values of E . Alternative methods of estimating the correct E values are suggested.

Kissinger plot for simulated data ($E = 100 \text{ kJ} \cdot \text{mol}^{-1}$)



Is the Kissinger Equation Applicable to the Processes that Occur on Cooling?

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Keywords: activation energy; crystallization; differential scanning calorimetry (DSC); kinetics; melt

Introduction

The method of Kissinger^[1] allows the activation energy, E to be determined from Equation (1)

$$\frac{d \ln \left(\frac{\beta}{T_p^2} \right)}{d \left(\frac{1}{T_p} \right)} = - \frac{E}{R} \quad (1)$$

where R is the gas constant, T_p is the temperature corresponding to the maximum of a differential kinetic curve at a given heating rate:

$$\beta = \frac{dT}{dt} \quad (2)$$

Equation (1) is easily solved as linear regression

$$\ln \left(\frac{\beta_i}{T_{p,i}^2} \right) = \text{Const} - \frac{E}{RT_{p,i}} \quad (3)$$

where i is the ordinal number of the run carried out at the heating rate, β_i . By using differential scanning calorimetry (DSC) and/or differential thermal analysis (DTA) one readily determines the values of T_p as “peak temperatures”. Both experimental and computational simplicity make Kissinger’s method a very popular procedure for kinetic evaluations of DSC and DTA data.

A number of recent applications of the Kissinger method have been concerned with nonisothermal crystallization of the polymer melts.^[2–20] The process is conducted by cooling the melt at a controlled cooling rate. On cooling the temperature decreases with time giving rise to negative values of β in Equation (2). Obviously, Equation (1) and (3) does not permit substitution of negative values for β . In the aforementioned melt crystallization studies, this problem has been avoided by dropping the minus sign in the negative heating rates. Note that this may happen inadvertently as some workers use the symbol β to denote the cooling rate, which is obviously positive. It should, however, be stressed that β in Equation (1) is invariably the heating rate.

The problem arises whether replacing negative heating rates with positive cooling rates in the Kissinger equation is a valid procedure? We feel that analysis of this problem is urgently needed because, without any justification, the procedure appears to develop rapidly into a “standard” approach to estimating the activation energy for crystallization of polymer melts. This paper provides the results of our analysis of the aforementioned problem.

Mathematics of the Kissinger Method

The Kissinger equation (1) is derived from the basic rate equation^[21]

$$\frac{da}{dt} = A \exp\left(\frac{-E}{RT}\right) f(a) \quad (4)$$

where a is the extent of conversion, t is the time, A is the preexponential factor, $f(a)$ is the reaction model. Taking the derivative of Equation (4) and setting it to zero, we obtain

$$\frac{d}{dt} \left(\frac{da}{dt} \right) = \frac{da}{dt} \left[\frac{E}{RT_p^2} \cdot \frac{dT}{dt} + \frac{df(a_p)}{da} \right] A \exp\left(\frac{-E}{RT_p}\right) = 0 \quad (5)$$

where subscript p denotes the values at the point of the rate maximum (peak). In Equation (5) the rate of temperature variation, dT/dt takes positive values for heating and negative values for cooling. In thermal analysis experiments the temperature is usually varied at a constant rate, β . The value β is traditionally called the heating rate (c.f., Kissinger^[11]). Regardless of its name, the sign of β is determined by the sign of the respective derivative (2). Substituting β for dT/dt into Equation (5) and the reaction order model, $(1-a)^n$, for $f(a)$ one obtains Equation (6)

$$\frac{d}{dt} \left(\frac{da}{dt} \right) = \frac{da}{dt} \left[\frac{E\beta}{RT_p^2} - n(1-a_p)^{n-1} \right] A \exp\left(\frac{-E}{RT_p}\right) = 0 \quad (6)$$

which is the equation that Kissinger originally used to arrive at Equation (1). Although Kissinger derived his equation assuming the reaction order kinetics, it can be demonstrated that Equation (1) holds for a wide class of the $f(a)$ functions. Because in Equation (5) da/dt is not zero, the left hand side becomes zero when:

$$\frac{E}{RT_p^2} \cdot \frac{dT}{dt} + \frac{df(a_p)}{da} A \exp\left(\frac{-E}{RT_p}\right) = 0 \quad (7)$$

Simple rearrangements of Equation (7) yield Equation (8)

$$\frac{\beta}{T_p^2} = - \frac{df(a_p)}{da} \cdot \frac{AR}{E} \exp\left(\frac{-E}{RT_p}\right) \quad (8)$$

that after the logarithmic transformation turns into Equation (1) and/or Equation (3) assuming that a_p is independent of β . Theoretically^[22] a_p should show a minor variation with β that can usually be neglected for practical purposes.

Let us now analyze Equation (8) for the conditions of heating and cooling. For heating the left hand side in Equation (8) is positive. For a regular chemical process A and E are positive, and the exponential function is always positive by definition. Subject to all these conditions Equation (7) holds on heating when the $f(a)$ derivative is negative. Therefore the right hand side in Equation (8) is positive. We can apply the logarithmic transformation to both sides of Equation (8) and obtain Equation (1) and/or Equation (3).

On cooling, the left hand side of Equation (8) is negative and so is the first term in Equation (7). Therefore, Equation (7) holds on cooling when the $f(a)$ derivative is positive. This makes both sides of Equation (8) negative and unsuitable for the logarithmic transformation. As mentioned earlier, this problem has been avoided by dropping the negative sign for β . Mathematically, this procedure is equivalent to reversing the signs of both sides of Equation (8) that results in Equation (9)

$$\frac{-\beta}{T_p^2} = \frac{df(a_p)}{da} \cdot \frac{AR}{E} \exp\left(\frac{-E}{RT_p}\right) \quad (9)$$

both sides of which are positive and suitable for the logarithmic transformation that ultimately leads to the standard Kissinger equation in its either form (1) or (3). Note that the resulting positive value $-\beta$ can be called the cooling rate.

The question arises whether the procedure of reversing the sign is valid. At the first sight it looks perfectly valid as it does not violate Equation (5). However, Equation (5) is not the sufficient condition of maximum. The sufficient condition includes both Equation (5) and inequality (10)

$$\frac{d}{dt} \left\{ \frac{da}{dt} \left[\frac{E}{RT_p^2} \cdot \frac{dT}{dt} + \frac{df(a_p)}{da} A \exp\left(\frac{-E}{RT_p}\right) \right] \right\} < 0 \quad (10)$$

which specifies that we are looking for the rate maximum. This rather complicated inequality has a very simple meaning that if at T_p the rate peak points upward, then Equation (5) satisfies the condition of maximum. The upward rate peaks obviously represent the most common experimental situation regardless of whether the process rate passes through a maximum on heating (e.g., decomposition) or on cooling (e.g., crystallization). As a matter

of fact, Equation (4) cannot give rise to any downward peaks as long as A and $f(a)$ remain positive (i.e., physically meaningful). For this reason Equation (5) as well as derived from it Equation (8) are equations of maximum.

On the other hand, Equation (9) is obtained by reversing the signs in Equation (8) that is equivalent to reversing the signs in Equation (5) as follows:

$$\frac{d}{dt} \left(\frac{da}{dt} \right) = \frac{da}{dt} \left[-\frac{E}{RT_p^2} \cdot \frac{dT}{dt} - \frac{df(a_p)}{da} \right]$$

$$A \exp \left(\frac{-E}{RT_p} \right) = 0 \quad (11)$$

Because the function in the brackets of Equation (11) is a mirror image of the respective function in Equation (5), Equation (11) is an equation of minimum and so is Equation (9). This means that Equation (9) requires the process rate to pass through a minimum, i.e., to yield a downward rate peak. This requirement contradicts the basic rate Equation (4). It can be shown that in order to arrive at Equation (11) one needs to reverse the sign of the right hand side of Equation (4). This requirement also contradicts experimental observations for crystallization of polymer melts, whose rate passes through a maximum and gives rise to an upward peak. Therefore, dropping the negative sign for β in order to make the Kissinger equation applicable to cooling processes is an invalid procedure.

Simulated Example

Let us estimate what may be a potential effect of using the positive values of cooling rates in the Kissinger equation on the values of the effective activation energy. As the only process whose kinetic parameters are known precisely is a simulated process, we have simulated a simple process whose rate obeys Equation (4) with following parameters: $E = 100 \text{ kJ} \cdot \text{mol}^{-1}$, $A = 10^{10} \text{ min}^{-1}$, and $f(a) = 4(1-a)[- \ln(1-a)]^{3/4}$ (the differential form of the Avrami equation with $n = 4$). The resulting rate equation has been integrated by using the Runge-Kutta method of 4th order^[23] to calculate the a vs t and da/dt vs t dependences. Integration was performed at three rates of temperature variation, β , which were -1 , -2 , and $-4 \text{ } ^\circ\text{C} \cdot \text{min}^{-1}$. The obtained rate peaks and the respective peak temperatures are shown in Figure 1. The values of T_p and $-\beta$ were substituted into Equation (3). The resulting Kissinger plot is shown in Figure 2. It is seen that the plot has a positive slope that means that the activation energy is negative. Its value is $-328.3 \text{ kJ} \cdot \text{mol}^{-1}$. Obviously this value differs dramatically from the value $100 \text{ kJ} \cdot \text{mol}^{-1}$ that we used to simulate the data.

This example shows that the use of positive values for cooling rates in the Kissinger equation may produce totally incorrect values of the effective activation energy.

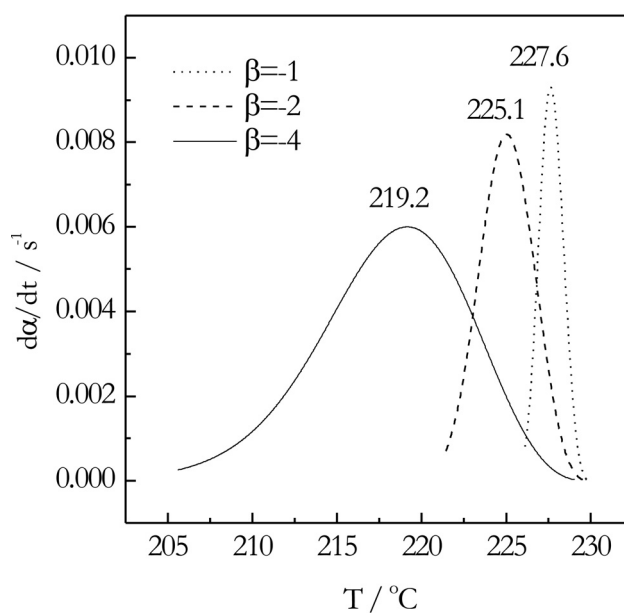


Figure 1. Simulated rate data. The numbers at the peaks are the peak temperatures in $^\circ\text{C}$.

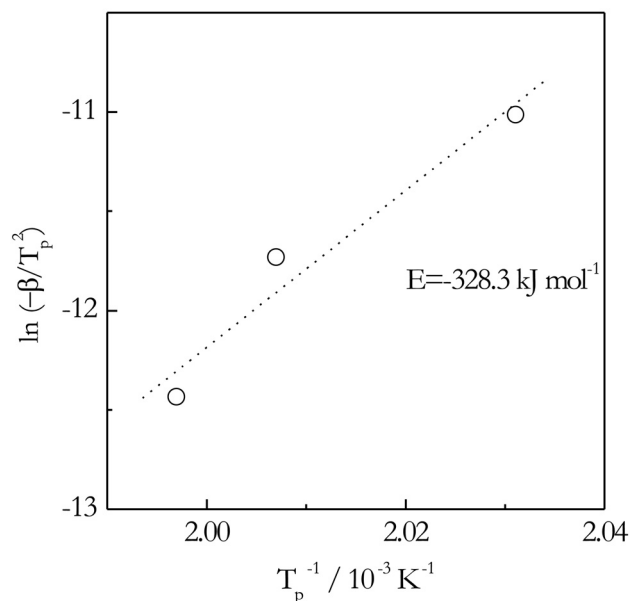


Figure 2. Kissinger plot for simulated data.

The next section describes two methods that can be applied for obtaining the correct values.

Alternative Methods of Evaluation

For processes that occur on cooling, reliable values of the effective activation energy can be obtained, for instance, by the differential isoconversional method of Friedman^[24] and/or by the integral isoconversional method of Vyazovkin.^[25,26] The Friedman equation is obtained by rearranging the basic rate Equation (4) as follows

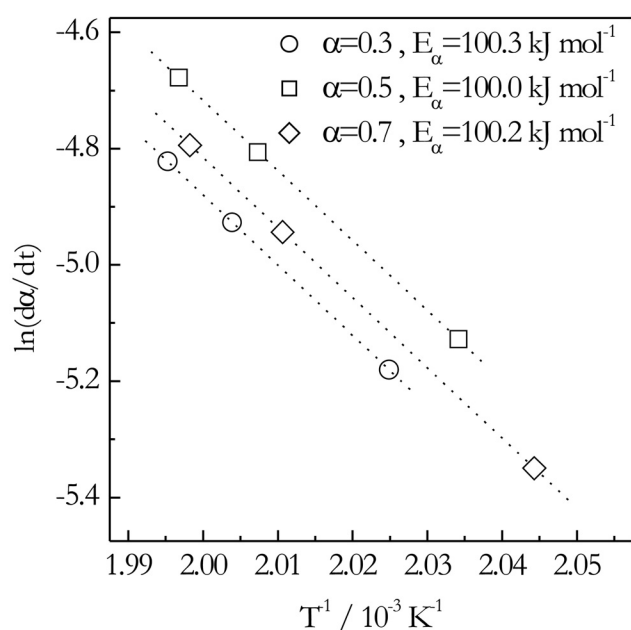


Figure 3. Friedman plots for simulated data.

$$\ln\left(\frac{d\alpha}{dt}\right)_{a,i} = \ln[Af(\alpha)] - \frac{E_a}{RT_{a,i}} \quad (12)$$

where the subscript a denotes the values related to a given extent of conversion and i is the ordinal number of the run carried out at the heating rate, β_i . The rate can be conveniently determined from DSC data. The measured rate of heat release is assumed to be proportional to the reaction rate

$$\frac{dQ}{dt} = Q_{rxn} \frac{d\alpha}{dt} \quad (13)$$

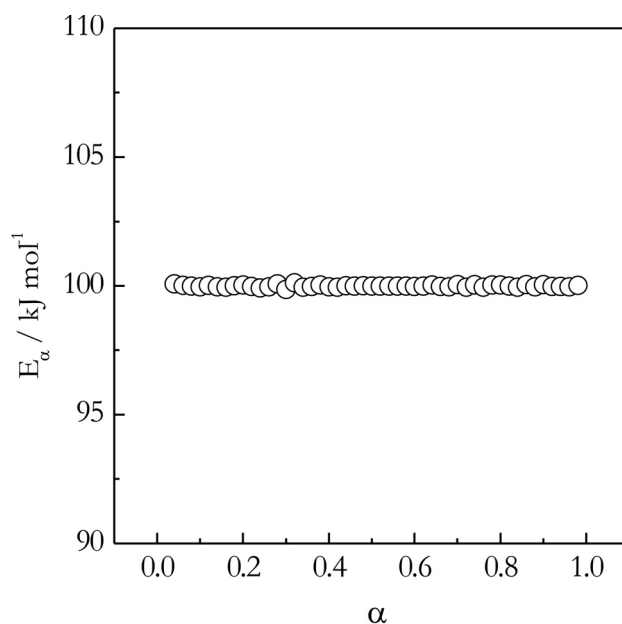
where Q_{rxn} is the measured reaction heat. The value of Q_{rxn} is determined by integration of a DSC peak. The values of Q_{rxn} can further be used to determine the crystallization rate, $\frac{d\alpha}{dt}$ as well as the extent of conversion:

$$\alpha = \frac{1}{Q_{rxn}} \int_0^t \frac{dQ}{dt} dt \quad (14)$$

Vyazovkin has used the integral form of Equation (4) to develop an advanced isoconversional method.^[25, 26] This method has been designed to treat the kinetics that occur under arbitrary variation in temperature. For a series of n experiments carried out under different temperature programs, $T_i(t)$, the activation energy is determined at any particular value of α by finding E_a , which minimizes the function

$$\Phi(E_a) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_a, T_i(t_a)]}{J[E_a, T_j(t_a)]} \quad (15)$$

where

Figure 4. E_a -dependence obtained from simulated data by using the method developed by Vyazovkin.Table 1. Experimental parameters of DSC peaks for crystallization of PET melt.^[32]

β °C · min ⁻¹	-3	-4	-6	-8	-12
$\frac{T_p}{^\circ\text{C}}$	213.1	209.6	208.1	206.9	201.6

$$J[E_a, T_i(t_a)] \equiv \int_{t_a - \Delta a}^{t_a} \exp\left[\frac{-E_a}{RT_i(t)}\right] dt \quad (16)$$

In Equation (16) α varies from Δa to $1 - \Delta a$ with a step $\Delta a = m^{-1}$, where m is the number of intervals chosen for analysis. The integral, J in Equation (16) is evaluated numerically by using the trapezoid rule.

The application of the Friedman equation to the simulated data gives the linear plots shown in Figure 3. The equation was applied to the rates at 3 arbitrarily chosen extents of conversion, 0.3, 0.5, and 0.7. It is seen that the obtained values of the effective activation energy are practically identical with the E value used in simulations. The use of the method developed by Vyazovkin yields a set of E_a shown in Figure 4. Again, the estimated values of E_a are practically identical with the E value used in simulations.

Evaluation of the effective activation energy as a function of the extent of conversion has an additional benefit of detecting changes in the process mechanism^[27] that are likely to occur in such complex processes as polymer crystallization.^[28–31] In particular the E_a -dependence has recently been found and interpreted for crystallization of PET melt.^[32]

Experimental data (Table 1) of our study^[32] can be used to obtain the Kissinger estimate of the effective activation

energy according to Equation (9). By plotting the data from Table 1 as $\ln(-\beta/T_p^2)$ against T_p^{-1} we obtain the value of $E = -261.2 \text{ kJ mol}^{-1}$. Since for these data^[32] the rate maximum of the DSC curves is found at a practically constant value $\alpha_p = 0.55$, the obtained Kissinger estimate should be associated with this extent of conversion. However, by using the advanced isoconversional method (Equation (15) and (16)), we have obtained^[32] the value $E_{0.55} = -169.5 \text{ kJ mol}^{-1}$ for this extent of conversion which is significantly larger than the Kissinger estimate.

Conclusions

The Kissinger equation appears to be generally inapplicable for evaluating the activation energy of the processes that occur on cooling. The use of this method with positive values of the cooling rate may result in erroneous values of the activation energy. The correct values can be determined by using the isoconversional methods developed by Friedman and by Vyazovkin. It would be highly advisable to apply these methods for recalculating the values of E reported in numerous papers that apply the Kissinger equation to the processes that occur on cooling.

Acknowledgement: Discussions of the problem with Drs. Joseph Flynn and Nicolas Sbirrazzuoli are gratefully acknowledged.

Received: July 15, 2002

Revised: August 7, 2002

Accepted: August 9, 2002

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