

## ON THE CALCULATION OF ACTIVATION ENERGIES USING A MODIFIED KISSINGER METHOD

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(Received May 7, 1979)

Augis and Bennett (*J. Thermal Anal.* 13 (1978) 283.) [6] recently proposed a modified Kissinger method for determining the activation energy of a transformation. It is shown that the proposed method was, in fact, based upon a modification to the equation for the rate of reaction under non-isothermal conditions. The apparent discrepancy between the proposed method and the original Kissinger method is therefore resolved. The modified rate equation appears to have, at best, only a limited application. However, if the equation should be appropriate for a particular transformation, it is demonstrated that Augis and Bennett's method would be the correct method for determining the activation energy.

The so-called peak-displacement or Kissinger [1] method of quantitative thermal analysis has often been used to determine the activation energies of the rate controlling processes for solid state transformations. The method involves the measurement of the temperature  $T_m$ , corresponding to the maximum rate of reaction during heating from an initial temperature  $T_0$ , at a constant heating rate,  $r$ . The temperature  $T_m$  can be equated to the maximum of an exothermic DTA peak if the specimen is in good thermal contact with the rest of the thermal analysis system [2]. If the thermal contact is poor it is necessary to relate the fraction transformed,  $x$ , to the observed differential temperature,  $\delta T$ , by means of a calibration constant. This constant may involve a linear [3, 4] or a quadratic [5] expression for  $x$  in terms of  $\delta T$ . The activation energy  $Q$ , for  $Q/RT_m \gg 1$  where  $R$  is the gas constant, is given by  $d[\ln(r/T_m^2)]/d(1/T_m)$  which is the gradient of the straight line obtained on plotting  $\ln(r/T_m^2)$  versus  $1/T_m$ .

In a recent paper, Augis and Bennett [6] proposed that  $Q$  should be calculated by plotting  $\ln[r/(T_m - T_0)]$  versus  $1/T_m$  for  $Q(T_m - T_0)/RT_m^2 \gg 1$ . In the limiting case of small  $T_0$  (i.e.  $(T_m - T_0)/T_m \approx 1$ ) there would seem to be serious discrepancy between the Augis–Bennett procedure and the conventional Kissinger procedure. The present communication will demonstrate that the discrepancy is an apparent one which arises because of differences in the assumed expression for the instantaneous rate of reaction under non-isothermal conditions. Having clarified this fundamental point it will be shown that the Augis–Bennett analysis contains important errors but that in spite of these errors, their proposed procedure is nonetheless correct for the assumed reaction rate law.

### Analysis

Consider first the conventional Kissinger method, the theoretical basis of which has been reviewed recently by Henderson [2] and others [7, 8]. These various authors have shown that the method gives a reasonably accurate estimate of the activation energy for a single, thermally activated process provided  $dx/dt$  is given by a generalized rate expression of the form:

$$dx/dt = f(x)g(T) \quad (1)$$

where  $dx/dt$  is the instantaneous rate of change with time of the fraction transformed, under non-isothermal conditions, and is a product of separate functions,  $f(x)$  and  $g(T)$ , of  $x$  and  $T$ . Integrating Eq. (1) from  $x = 0$  to  $x = x_m$  yields:

$$\int_0^{x_m} \frac{dx}{f(x)} = h(x_m) \quad \text{say} = \frac{1}{r} \int_{T_0}^{T_m} g(T)dT \quad (2)$$

where  $x_m$  is the fraction transformed at  $T_m$ . If it can be shown that  $h(x_m)$  is independent of  $r$  (i.e., the fraction transformed at  $T_m$  is the same for all linear heating rates), we can evaluate  $Q$  by integrating an assumed expression for the rate function,  $g(T)$ . The usual assumption [2, 7, 8] is that  $g(T)$  is given by an Arrhenius equation of the form:

$$g(T) = k \exp(-Q/RT) \quad (3)$$

where  $k$  is a frequency factor. Hence, for a sufficiently small  $T_0$  and  $Q/RT \gg 1$  it can be shown [9, 10] that:

$$h(x_m) = (k/r) \int_{T_0}^{T_m} \exp(-Q/RT)dT \approx (RT_m^2 k/rQ) \exp(-Q/RT) \quad (4)$$

where the asymptotic expansion for the exponential-integral function has been cut off at the first term. Thus, if  $h(x_m)$  is independent of the heating rate,  $Q$  can be estimated by plotting  $\ln(r/T_m^2)$  versus  $1/T_m$ .

That the temperature  $T_m$  corresponds to equal fractions transformed can be demonstrated as follows: a maximum requires  $d^2x/dt^2 = 0$  so from Eq. (1) we have,

$$\frac{df(x_m)}{dx} + \frac{r}{[g(T)]^2} \frac{dg(T)}{dT} = 0. \quad (5)$$

Using Eq. (3) and Eq. (4) it can be demonstrated that this condition corresponds to:

$$\frac{df(x_m)}{dx} + \frac{1}{h(x_m)} \approx 0. \quad (6)$$

Equation (6) is in  $x_m$  only so its solution is independent of the heating rate and the maxima at  $T_m$  correspond to equal fractions transformed.

Consider, on the other hand, the Augis-Bennett analysis. In this case, it is observed that Eq. (8) of Augis and Bennett's paper reads as follows:

$$dx/dt = (du/dt)n u^{n-1}(1-x) \quad (7)$$

where  $n$  is the rate exponent appearing in the Avrami equation for isothermal transformation:

$$x = 1 - \exp[-(Kt)^n] \quad (8)$$

and

$$u = Kt = tk \exp(-Q/RT). \quad (9)$$

Equation (7) for the non-isothermal rate of reaction can be rewritten by noting that:

$$\begin{aligned} du/dt &= k \exp(-Q/RT)[1 + rQ/RT^2] \\ &= k \exp(-Q/RT)[1 + Q(T - T_0)/RT^2] \end{aligned} \quad (10)$$

where  $(T - T_0) = rt$ . Substituting for  $du/dt$  Eq. 10 and for  $u$  using Eqs (8) and (9) shows that Eq. (7) becomes:

$$dx/dt = n[-\ln(1-x)]^{\frac{n-1}{n}}(1-x)k[1 + Q(T - T_0)/RT^2] \exp(-Q/RT). \quad (11)$$

This is an equation in  $x$  and  $T$  such that Augis and Bennett's generalized rate functions  $f(x)$  and  $g(T)$ , for non-isothermal transformation are given by:

$$g(T) = k[1 + Q(T - T_0)/RT^2] \exp(-Q/RT) \quad (12)$$

$$f(x) = n[-\ln(1-x)]^{\frac{n-1}{n}}(1-x) \quad (13)$$

Clearly, for  $Q(T - T_0)/RT^2 \ll 1$ , Eq. (12) reduces to:

$$g(T) = k \exp(-Q/RT) \quad (14a)$$

and for  $Q(T - T_0)/RT^2 \gg 1$ , we have

$$\begin{aligned} g(T) &= k[Q(T - T_0)/RT^2] \exp(-Q/RT) \\ &= (kQ/RT) \exp(-Q/RT) \text{ for } T_0 = 0. \end{aligned} \quad (14b)$$

It is therefore not unsurprising that for  $T_0 = 0$  and  $Q/RT \gg 1$  there is an apparent conflict between the results of Augis and Bennett's analysis and the results of earlier analyses [2, 7, 8] of the Kissinger method. The latter were based on the use of an Arrhenius rate function (Eq. 14a) as opposed to Augis and Bennett's modified expression (Eq. 14b) for  $g(T)$ .

Turning now to the details of the analysis presented by Augis and Bennett, it is noted that these authors did not follow the usual scheme for determining the con-

ditions to be satisfied at  $T_m$ . Instead, they evaluated the first term appearing in Eq. (5) by differentiating Eq. (13) to give  $df(x)/dx$  and substituting for  $x_m$  using Avrami's isothermal transformation law (Eq. 8). This is an invalid approach because the Avrami law cannot be used to estimate  $x_m$  during non-isothermal transformations.

A valid analysis for Augis and Bennett's modified rate law (Eq. 11) can be carried out by employing the approach described earlier for the Kissinger method. However, before performing this analysis, it should be pointed out that Augis and Bennett's paper contains a mathematical mistake wherein the expression for  $d^2u/dt^2$  (page 285 of their paper) should include the following additional term:

$$-u(2ar/T)$$

where the parameter  $a$  is equal to  $Qr/RT^2$ . It is important to emphasise that the incorporation of this term does not rectify Augis and Bennett's analysis but merely corrects a mathematical error.

Adopting the procedure outlined above for the Kissinger method, we note that Augis and Bennett's rate function (Eq. 12) for  $T_0 = 0$  can be integrated and substituted in Eq. 2 to give:

$$h(x_m) = (k/r) \int_0^{T_m} (1 + Q/RT) \exp(-Q/RT) dt \approx (T_m k/r) \exp(-Q/RT_m) \quad (15)$$

for  $Q/RT \gg 1$ . This integral has been evaluated using (9),

$$\int_{-\infty}^x (e^x/x) dx \approx e^{-x} [x^{-2} - x^{-1}] \text{ for } x \gg 1.$$

Moreover, by substituting Eq. (12) for  $g(T)$  in Eq. (5), the condition for a maximum, where  $T_0 = 0$  becomes:

$$\frac{df(x_m)}{dx} + \frac{r(Q/RT_m)^2}{k(1 + Q/RT_m)^2 T_m \exp(-Q/RT_m)} = 0.$$

Hence, for  $Q/RT_m \gg 1$ , we have

$$\frac{df(x_m)}{dx} + \frac{r}{T_m k \exp(-Q/RT_m)} \approx \frac{df(x_m)}{dx} + \frac{1}{h(x_m)} \approx 0. \quad (16)$$

The solution to Eq. 16 is independent of  $r$  and to the approximation implicit in Eq. 15, the maxima at  $T_m$  correspond to equal fractions transformed. Hence, we can use Eq. 15 to estimate  $Q$  by plotting  $\ln(r/T_m)$  versus  $1/T_m$ . Consequently, the  $\ln(r/T_m)$  plot (for  $Q/RT_m \gg 1$  and  $T_0 = 0$ ) proposed by Augis and Bennett is indeed the correct method for estimating the activation energy, for their assumed rate expression.

## Discussion

In the preceding analysis it has been shown that the conventional Kissinger method and the modified method of Augis and Bennett [2] can be reconciled if it is appreciated that the two methods are based upon different expressions for the rate function,  $g(T)$ , appearing in rate equation for transformation under non-isothermal conditions (Eq. 1). The theoretical basis for the equation has been considered recently by Henderson [2, 11] and by Gorbachev [12]. These authors pointed out that the equation is applicable to a limited number of transformations such as those involving site saturation (zero nucleation rate) with linear growth kinetics (growth rate independent of time). The equation may also be used as an approximation for those cases which do conform to the criteria specified by Henderson [2, 11]. It is also legitimate to replace the Arrhenius rate function,  $g(T)$ , by some other function of  $T$  which describes the reaction rate. For example, the rate of crystallization of a glass can often be described in terms of a Fulcher expression for the rate constant (i.e.,  $g(T) = \exp[-Q/R(T - T^*)]$  where  $T^*$  is a constant). It is relevant to note, however, that in the numerous reports dealing with measurements of kinetic parameters for solid-state transformations, there appears to have been no mention made of a parameter which is proportional to Augis and Bennett's modified rate function,  $g(T) = k(1 + Q/RT) \exp(-Q/RT)$ . Consequently, the adoption of a thermal analysis method based on this function must be expected to be inappropriate for the vast majority of solid-state transformations.

## Conclusion

1. A modification made by Augis and Bennett to the Kissinger, or peak-displacement, method of quantitative thermal analysis was based upon the use of a non-Arrhenius expression for the rate function appearing in the rate equation for transformation under non-isothermal conditions.
2. The adoption of the modified rate function means that the peak-displacement method can be used to estimate the activation energy,  $Q$ , for large  $Q/RT_m$  provided  $\ln(r/T_m)$  is plotted as a function of  $1/T_m$ . The parameters appearing in these terms are  $T_m$ , the temperature corresponding to the maximum rate of reaction;  $r$ , the linear heating rate; and  $R$ , the gas constant.
3. Augis and Bennett's proposed rate function, and their modified method, have only a limited application in the measurement of reaction rate parameters for solid-state transformations.

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The author is indebted to the Senate of the University of Queensland for the award of a University Research Fellowship; and to Professor R. R. Stephens for providing laboratory facilities.

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ZUSAMMENFASSUNG — Von Augis und Bennett (*J. Thermal Anal.* 13, (1978) 283) wurde eine modifizierte Kissinger-Methode zur Bestimmung der Aktivierungsenergie einer Umwandlung vorgeschlagen. Es wird gezeigt, dass die vorgeschlagene Methode tatsächlich in einer Modifizierung der Gleichung für die Reaktionsgeschwindigkeit unter nicht-isothermen Bedingungen ihren Ursprung hat. Die scheinbare Diskrepanz zwischen der vorgeschlagenen Methode und der ursprünglichen Kissinger-Methode wird dadurch behoben. Die modifizierte Geschwindigkeitsgleichung hat bestenfalls nur eine begrenzte Anwendung. Jedoch, bei Eignung dieser Gleichung für eine bestimmte Umwandlung zeigt sich, dass die Methode von Augis und Bennett die richtige Methode zur Bestimmung der Aktivierungsenergie sein kann.

Резюме — Огис и Беннетт (*J. Thermal Anal.* 13 (1978) 283.) недавно предложили видоизмененный метод Киссинджера для определения энергии активации какого-либо превращения. Показано, что предложенный метод, в действительности, основан на видоизмененном уравнении скорости реакции в неизотермических условиях. Следовательно, разрешено кажущееся противоречие между предложенным методом и подлинным методом Киссинджера. Кажется, что видоизмененное уравнение скорости, в лучшем случае, может иметь только ограниченное значение. Показано, что если уравнение предназначено для специфического превращения, то метод Огиса и Беннетта может быть корректным методом для определения энергии активации.