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Thermochimica Acta 298 (1997) 149–153

thermochimica
acta

On the determination of kinetic parameters by using points of inflection of a DTA curve

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Received 6 June 1996; accepted 2 January 1997

Abstract

It has been demonstrated that points of inflection of a differential thermal analysis (DTA) peak can indicate its order of kinetics. A new set of expressions involving peak temperature T_m and temperature T_{i1} and T_{i2} corresponding to the points of inflection have been obtained for the evaluation of activation energy. The validity of these expressions is discussed by applying them to a number of DTA curves. © 1997 Elsevier Science B.V.

Keywords: Activation energy; Kinetics; Point of inflection; Pre-exponential factor

1. Introduction

Differential thermal analysis (DTA) is an indispensable tool for the study of complex chemical reactions. Moreover, DTA curves are often used for the quantitative identification of organic and inorganic compounds. In the literature there are various methods for the determination of the kinetic parameters. These methods have been reviewed by Chen and Kirsh [1], Chen [2], Mendlandt [3] and Blazek [4]. Recently, Luo [5] has proposed a method of calculation of the kinetic parameters of a DTA curve by using some characteristic temperatures which also include the temperature at one of the points of inflection. He has, however, not evaluated the temperature integral accurately. Although the method of Luo [5] eliminates the difficulties encountered in earlier works [6,7], his expressions for the evaluation of activation energy and order of kinetics still have some restrictions. In the present paper we report a number of expressions for the determination of the activation energy of DTA curve with arbitrary order of kinetics ($0.5 \leq n \leq 3$). These expressions involve the peak temperature T_m and/or temperature T_{i1} and T_{i2} corresponding to the two points of inflection. We have also shown that the points of inflection of a DTA curve can indicate its order of kinetics.

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0040-6031/97/$17.00
PII S0040-6031(97)00152-4

2. Theory

Following Luo [5] the expression for the solid state decomposition reaction of the nth order can be written as

$$\frac{dx}{dt} = A(1-x)^n \exp(-E/RT) \tag{1}$$

where x is the fraction of the reaction completed in time t, A is the pre-exponential factor, R is the universal gas constant and E is the activation energy. In a DTA curve the temperature deviation ΔT from the horizontal base line can be expressed as

$$\Delta T = \beta \frac{dx}{dt} \tag{2}$$

where β is the proportionality constant. From Eqs. (1) and (2) we get after some algebraic simplification

$$\Delta T = A\beta \left[1 + (n-1)\frac{A}{\Phi}\int_{T_0}^{T} \exp(-E/RT')dT'\right]^{-n/(n-1)} \times \exp(-E/RT) \quad \text{for } n \neq 1 \tag{3}$$

and

$$\Delta T = A\beta \exp(-E/RT) \times \exp\left[-\frac{A}{\Phi}\int_{T_0}^{T} \exp(-E/RT')dT'\right] \quad \text{for } n = 1 \tag{4}$$

where Φ is the linear heating rate, T_0 is the starting temperature and T is the temperature at time t. At the peak temperature $T = T_m$ the deflection of DTA curve is maximum so that

$$\left[\frac{d\Delta T}{dT}\right]_{T=T_m} = 0. \tag{5}$$

From Eqs. (4) and (5) at $T = T_m$ one can write for $n = 1$

$$\frac{\Phi E}{RT_m^2} = A\exp(-E/RT_m). \tag{6}$$

Similarly for $n \neq 1$ one gets

$$1 + (n-1)\frac{A}{\Phi}\int_{T_0}^{T_m} \exp(-E/RT)dT = \frac{nA\,RT_m^2}{\Phi E}\exp(-E/RT_m). \tag{7}$$

The evaluation of the integral,

$$\int_{T_0}^{T} \exp(-E/RT')$$

popularly known as temperature integral, is not straightforward to evaluate. It is shown by Chen and Kirsh [2] that for a given value of the activation energy E, the temperature integral is a strongly increasing function of T so that

$$\int_{T_0}^{T} \exp(-E/RT')dT' \approx \int_{0}^{T} \exp(-E/RT')dT'. \tag{8}$$

Now following Gartia et al. [8] we get

$$\int_{0}^{T} \exp(-E/RT')dT' = \frac{E}{R}\frac{E_2(u)}{u} \tag{9}$$

where $u = E/RT$ and $E_2(u)$ is the second exponential integral [9]. Using Eqs. (3),(4) and (7) one can arrive at

$$\frac{\Delta T}{(\Delta T)_m} = \exp[u_m - u + F(u, u_m)] \quad \text{for } n = 1 \tag{10}$$

and

$$\frac{\Delta T}{(\Delta T)_m} = \exp(u_m - u) \times [1 - (n-1)/n\,F(u, u_m)]^{-n/(n-1)} \quad \text{for } n \neq 1 \tag{11}$$

with

$$F(u, u_m) = u_m^2 \exp(u_m)[E_2(u_m)/u_m - E_2(u)/u], \tag{12}$$

$(\Delta T)_m$ is the maximum value of ΔT and $u_m = E/RT_m$.

The points of inflection of a DTA peak curve at temperature T_{i1} and T_{i2} such that

$$\left[\frac{\mathrm{d}^2\Delta T}{\mathrm{d}T^2}\right]_{T=T_{i,j}\,(j=1,2)} = 0 \tag{13}$$

For $n = 1$ Eq. (13) can be expressed as

$$u\left[\frac{\mathrm{d}F}{\mathrm{d}u}-1\right]\frac{\mathrm{d}\Delta T}{\mathrm{d}u}+\left[2\left\{\frac{\mathrm{d}F}{\mathrm{d}u}-1\right\}+u\frac{\mathrm{d}^2F}{\mathrm{d}u^2}\right]\Delta T=0$$
$$\text{for } u = u_{i,j}\ (u_{i,j} = E/\mathrm{RT}_{i,j} \tag{14}$$

whereas for $n \neq 1$ we can write

$$2u\frac{\mathrm{d}\Delta T}{\mathrm{d}u} + (u+2)\Delta T - \exp(u_\mathrm{m}-u)\left[2\frac{\mathrm{d}G}{\mathrm{d}u}+u\frac{\mathrm{d}^2G}{\mathrm{d}u^2}\right] = 0 \tag{15}$$

for $u = u_{i,j}$, $G = D^{-n/(n-1)}$ and $D = 1 - (n-1)F/n$.

The points of inflection for first order ($n = 1$) and non-first order ($n \neq 1$) DTA peaks can be found out by solving Eqs. (14) and (15) numerically. Using the standard technique of linear regression [10] it is found that a good linear correlation exists between the following pairs of variables:$[u_\mathrm{m}, u_{i1}/(u_{i1}-u_\mathrm{m})]$, $[u_\mathrm{m}, u_{i2}/(u_\mathrm{m}-u_{i2})]$ and $[u_\mathrm{m}, u_{i1}u_{i2}/u_\mathrm{m}(u_{i1}-u_{i2})]$ with $u_{i,j} = E/\mathrm{RT}_{i,j}$, so that one can write

$$u_\mathrm{m} = A_1\frac{u_{i1}}{(u_{i1}-u_\mathrm{m})} + B_1 \tag{16}$$

$$u_\mathrm{m} = A_2\frac{u_{i2}}{(u_{i2}-u_\mathrm{m})} + B_2 \tag{17}$$

$$u_\mathrm{m} = A_3\frac{u_{i1}u_{i2}}{u_\mathrm{m}(u_{i1}-u_{i2})} + B_3 \tag{18}$$

where the coefficients A_k and B_k $(k = 1-3)$ occurring in Eqs. (16)–(18) depend on the order of kinetics. These three equations can be recast in the form

$$E = \frac{A_1\mathrm{RT}_\mathrm{m}^2}{(T_\mathrm{m}-T_{i1})} + B_1\mathrm{RT}_\mathrm{m} \tag{19}$$

$$E = \frac{A_2\mathrm{RT}_\mathrm{m}^2}{(T_{i2}-T_\mathrm{m})} + B_2\mathrm{RT}_\mathrm{m} \tag{20}$$

$$E = \frac{A_3\mathrm{RT}_\mathrm{m}^2}{(T_{i2}-T_{i1})} + B_3\mathrm{RT}_\mathrm{m}. \tag{21}$$

By using the technique of non-linear least square regression [11] each of the coefficients of A_k and B_k can be expressed as a quadratic function of n $(0.5 \leq n \leq 3.0)$ as

$$A_k = a_{0k} + a_{1k}n + a_{2k}n^2 \tag{22}$$

$$B_k = b_{0k} + b_{1k}n + b_{2k}n^2 \tag{23}$$

The coefficients a_{1k} and b_{1k} $(1 = 0-2)$ are presented in Table 1.

Table 1
Coefficients a_{1k} and b_{1k} occurring in Eqs. 24 and 25 for the determination of activation energy

k	a_{0k}	a_{1k}	a_{2k}	b_{0k}	b_{1k}	b_{2k}
1	0.8430	−1.5165	0.1184	0.4749	0.5461	−0.0620
2	0.9828	−1.8137	0.1381	0.4738	0.5476	−0.0626
3	0.9123	−1.6646	0.1287	0.9487	1.0937	−0.1246

3. Results and discussions

The temperature T_{i1} and T_{i2} corresponding to the points of inflection of numerically computed DTA peaks have been found out by solving Eqs. (14) and (15) numerically by the Newton–Raphson method [12]. This method is very sensitive to the initial guess values of T_{i1} and T_{i2}. In some cases we encounter difficulties of convergence and to overcome this problem we have used the bisection method following Press et al. [13]. For experimental DTA peaks T_{i1} and T_{i2} have been determined by using the cubic spline method [14,15].

In Figs. 1 and 2 we show the variation of $(\Delta T)_{i1}/(\Delta T)_\mathrm{m}$ and $(\Delta T)_{i2}/(\Delta T)_\mathrm{m}$ with $u_\mathrm{m} = E/\mathrm{RT}_\mathrm{m}$ for $10 \leq u_\mathrm{m} \leq 100$ corresponding to different values of n, namely $n = 0.7$, 1.0, 1.5, 2.0, 2.5. From these figures it is evident that the dependence of these ratios on u_m is not very strong and the maximum variation is about 7% for smaller values of u_m. For $u_\mathrm{m} \geq 20$ these ratios are almost independent of u_m. On the other hand, these ratios depend strongly on the order of kinetics n and hence be used to estimate the order of kinetics. In Fig. 3 we exhibit the dependence of the ratios $(\Delta T)_{ij}/(\Delta T)_\mathrm{m}$ $(j = 1,2)$ on the order of kinetics n for $u_m = 40$. It is clear from this figure that the ratio $(\Delta T)_{i2}/(\Delta T)_\mathrm{m}$ corresponding to the falling side $(j = 2)$ of the DTA peak is much more sensitive to the order of kinetics than that corresponding to the rising side. So we can determine the order of kinetics

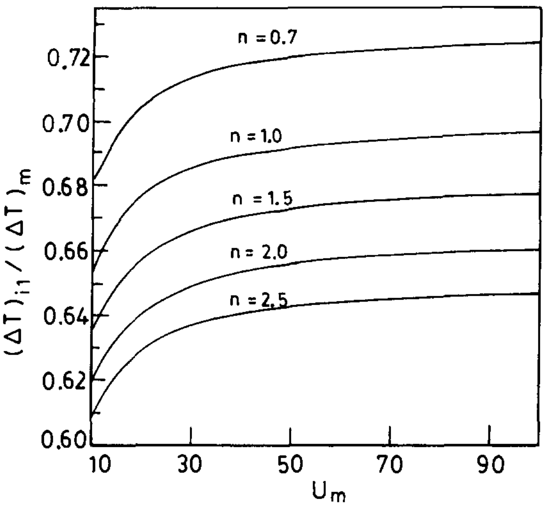

Fig. 1. Variation of $(\Delta T)_{i1}/(\Delta T)_m$ with u_m for different order of kinetics (n).

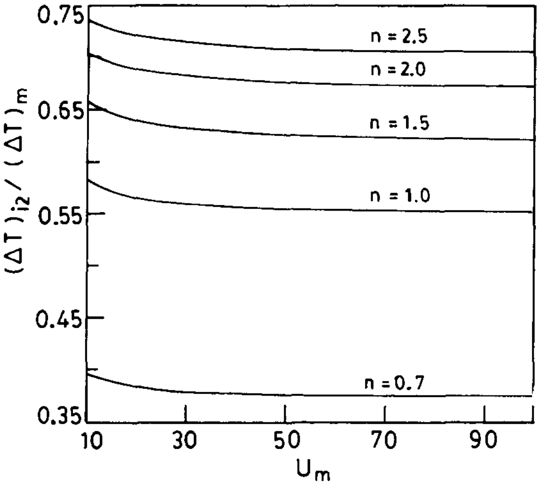

Fig. 2. Variation of $(\Delta T)_{i2}/(\Delta T)_m$ with u_m for different order of kinetics (n).

by using the curve connecting the ratio $(\Delta T)_{i2}/(\Delta t)_m$ and the order of kinetics n. The appropriateness of the order of kinetics so determined can be checked by observing whether the order of kinetics calculated by using both the curves in Fig. 3 are consistent.

Finally, we test the applicability of the present method by applying it to evaluate the kinetic parameters of a number of DTA curves selected from the literature, namely, those of calcitic limestone [6,16], georgia kaolinite [6,16], eureka halloysite [6,16], Cyclotrimethylenetrinitrame (RDX) [17] and trinitrotoluene (TNT) [17]. We denote the activation energies as calculated by using Eqs. (19)–(21) by E_1, E_2 and E_3 and E represent the average of these three values. These results are displayed in Table 2. The kinetic parameters calculated by the present method are in fair agreement with those reported in the literature.

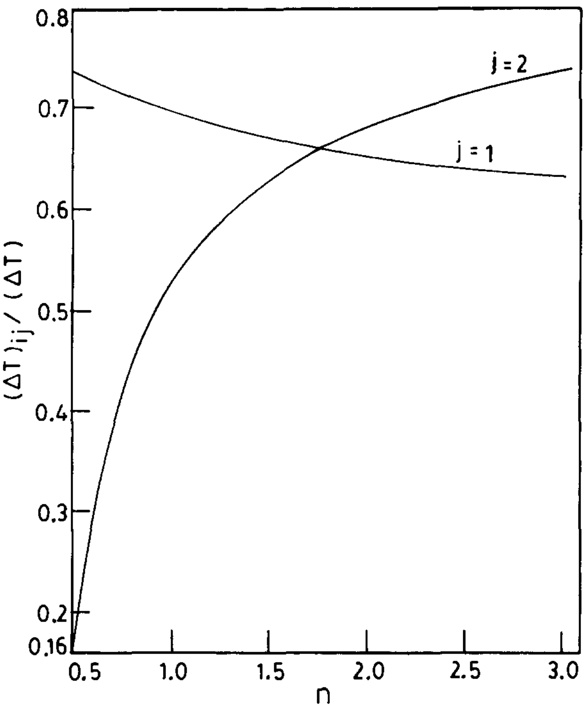

Fig. 3. Variation of $(\Delta T)_{ij}/(\Delta T)_m$ [j=1,2] with order of kinetics (n).

4. Conclusion

In the present paper we have reported a number of expressions from which one can determine the activation energy of a DTA peak once its points of inflection are known. We also show that the point of inflection of a DTA peak can indicate its order of kinetics. Finally the validity of the present method has been demonstrated by applying it to a number of experimental DTA peaks.

Table 2
Value of kinetic parameters of some experimental DTA peaks. a(b) stands for a×10^b.

System	Φ (°C min^{-1})	n	E_1 (K cal)	E_2 (K cal)	E_3 (K cal)	E (K cal)	A (sec^{-1})
Georgia kaolinite [6,16]	6	1.0	36.48	36.53	36.51	36.51	3.33(6)
Eureka halloysite [6,16]	6	1.0	37.82	37.64	37.83	37.76	5.05(7)
Calcitic limestone [6,17]	6	0.55	45.72	45.77	45.74	45.74	4.45(6)
Calcitic limestone [6,17]	15	0.56	45.72	45.51	45.73	45.65	4.14(6)
RDX[17]	6	0.85	45.33	44.77	45.05	45.05	2.33(17)
RDX[17]	15	0.96	46.21	45.95	46.58	46.58	7.13(17)
TNT[17]	6	1.65	21.94	21.96	21.96	21.95	6.78(5)
TNT[17]	10	1.75	20.99	20.99	20.99	20.99	2.87(5)

Acknowledgements

One of the authors (NCD) thanks the Department of Science and Technology (DST), Government of India, for financial assistance. The authors are grateful to Professor R.K. Gartia, Dr. Th Basanta Singh and Dr. T.K. Chakraborty for fruitful discussions.

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