Thermochimica Acta, 200 (1992) 293–297
Elsevier Science Publishers B.V., Amsterdam

Determination of the activation energy for a decomposition reaction from a single DSC curve

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(Received 22 January 1992)

Abstract

The area ratio concept and the characteristics of a thermogravimetric curve have been combined to derive the activation energy from a single DSC curve. The calculation is straightforward without any iteration and the results are in fair agreement with literature data.

INTRODUCTION

Differential scanning calorimetry (DSC) is widely applied, owing to its simplicity of operation. In particular, in the investigation of kinetic parameters of the decomposition reaction of substances, DSC is a simple and effective tool. Therefore, the objective of the following analysis is the calculation of the kinetic parameters from a DSC thermogram using a rapid, effective and convenient technique.

Rogers and Morris [1] derived the equation $E = R(\ln d_1/d_2)/(1/T_1 - 1/T_2)$ by the assumption of $n = 0$ for the linear Arrhenius plot. Their method is very simple, but the errors in the values calculated from this equation are larger than those obtained by other approaches [2]. Combining least-mean-squares and trial-and-error iterations, Hu et al. [3] obtained a method for calculating the kinetic parameters from a single DSC curve. The deficiency of this method, however, is that a reaction mechanism has to be assumed and a series of trial-and-error iteration procedures has to be performed in order to obtain the result. Both Flynn and Wall [4] and

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Ozawa [5] employed Doyle's [6] approximation to derive the equation $\Delta \log \beta/\Delta(1/T) \approx 0.475\ E/R$, where β is the rate of temperature increase. But this approach requires the use of multiple DSC curves at different rates of temperature increase.

When investigating the rapid calculation of the kinetic parameters of a decomposition reaction, the most frequently mentioned approach utilizes the approximation that the conversion rate is almost equal to the ratio of the area of the heat of an absorption (or desorption) peak to the total area of the thermogram. This concept was first introduced and applied to the calculation of the kinetic parameters of a reaction in solution (DTA method) by Borchardt and Daniels [7]. Later, Uricheck [8] applied this concept to calculate solid decomposition by DSC. Using the area ratio concept to calculate decomposition kinetic parameters, data from the original DSC curve must be used to draw another diagram in order to determine the slope and intercept [9,10]. This paper attempts to combine the area ratio concept and the characteristics of DSC curves to derive a direct method for the calculation of kinetic parameters.

THEORETICAL CONSIDERATIONS

Heat flow versus temperature data can be obtained from a single DSC thermogram as follows. Assuming the heat flow is proportional to the reaction rate

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \beta \frac{\mathrm{d}X}{\mathrm{d}t} \tag{1}$$

where β is a proportionality constant, $\mathrm{d}H/\mathrm{d}t$ is the heat flow and $\mathrm{d}X/\mathrm{d}t$ is the reaction rate.

By integrating eqn. (1), we obtain

$$\beta \int_0^1 \mathrm{d}X = \int_0^{\Delta H_0} \left(\frac{\mathrm{d}H}{\mathrm{d}t} \right) \mathrm{d}t = \Delta H_0 \tag{2}$$

i.e. the proportionality constant β is equal to the heat released during the reaction process ΔH_0. For ordinary decomposition reactions, the reaction rate is represented by $\mathrm{d}X/\mathrm{d}t = A(1-X)^n \exp(-E/RT)$. Therefore the heat flow can be expressed as

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \Delta H_0 A\ \mathrm{e}^{-E/RT}(1-X)^n \tag{3}$$

where X, t, A, n, E, R and T represent the fraction of the material reacted, the time, the pre-exponential factor of the Arrhenius equation, the reaction order, the activation energy, the gas constant and the absolute temperature respectively.

Taking logarithms and letting $q = \mathrm{d}H/\mathrm{d}t$, then differentiating with respect to temperature, one obtains

$$\frac{\mathrm{d}\ln q}{\mathrm{d}T} = \frac{E}{RT^2} - \frac{n}{1-X}\frac{\mathrm{d}X}{\mathrm{d}T} \tag{4}$$

or

$$\frac{\mathrm{d}q/\mathrm{d}T}{q} = \frac{E}{RT^2} - \frac{n}{1-X}\frac{\mathrm{d}X}{\mathrm{d}T} \tag{5}$$

If a constant heating rate is applied ($T = T_0 + \Phi t$, where Φ is the heating rate) to the operational process, then eqn. (5) can be rearranged as follows:

$$\frac{\mathrm{d}q}{\mathrm{d}T} = \frac{E}{RT^2}q - \frac{n}{1-X}\frac{1}{\Phi\,\Delta H_0}q^2 \tag{6}$$

Ozawa [11] and Horowitz and Metzger [12] have pointed out that the conversion rate "at the reaction peak" is a constant. Therefore it is reasonable to select a characteristic point on the curve for the calculation of the reaction kinetic parameters. In fact, Yang and Steinberg [13] and Liu et al. [14] have used the characteristic points (the maxima and reflecting point) of a curve to develop a method for the calculation of reaction kinetic parameters. Because the first-order derivative is equal to zero at the peaks of a curve, i.e. $\mathrm{d}q/\mathrm{d}t = 0$ when $T = T_\mathrm{m}$ (T_m is the peak temperature), and also, from eqn. (2)

$$X = \frac{1}{\Delta H_0}\int_0^t \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t = \frac{\Delta H}{\Delta H_0} \tag{7}$$

From eqn. (6), we obtain

$$\frac{E}{RT_\mathrm{m}^2} - \frac{n}{\Delta H_0 - \Delta H_\mathrm{m}}\frac{q_\mathrm{m}}{\Phi} = 0 \tag{8}$$

When eqn. (6) is differentiated with respect to temperature, a second-order derivative of heat flow versus temperature is obtained:

$$\frac{\mathrm{d}^2 q}{\mathrm{d}T^2} = \frac{E}{RT^2}\frac{\mathrm{d}q}{\mathrm{d}T} - \frac{2Eq}{RT^3} - \frac{nq^3}{\Phi^2\,\Delta H_0^2(1-X)^2} - \frac{2nq}{(1-X)\Phi\,\Delta H_0}\frac{\mathrm{d}q}{\mathrm{d}T} \tag{9}$$

The second-order derivative, eqn. (9), equals zero at the inflection point ($T = T_\mathrm{i}$) of the curve, and substituting eqns. (6) and (8) into eqn. (9), we obtain

$$\left(\frac{E}{RT_\mathrm{i}^2}\right)^2 q_\mathrm{i} - \frac{3(\Delta H_0 - \Delta H_\mathrm{m})}{\Delta H_0 - \Delta H_\mathrm{i}}\frac{E^2}{(RT_\mathrm{i}T_\mathrm{m})^2}\frac{q_\mathrm{i}^2}{q_\mathrm{m}} - \frac{2Eq_\mathrm{i}}{RT_\mathrm{i}^3}$$
$$- \frac{(\Delta H_0 - \Delta H_\mathrm{m})}{\Phi(\Delta H_0 - \Delta H_\mathrm{i})^2}\frac{q_\mathrm{i}^3}{q_\mathrm{m}}\frac{E}{RT_\mathrm{m}^2} + \frac{2(\Delta H_0 - \Delta H_\mathrm{m})^2}{(\Delta H_0 - \Delta H_\mathrm{i})^2}\frac{E^2}{R^2T_\mathrm{m}^4}\frac{q_\mathrm{i}^3}{q_\mathrm{m}^2} = 0 \tag{10}$$

If $\alpha = (\Delta H_0 - \Delta H_m)/(\Delta H_0 - \Delta H_i)$, and $\gamma = q_i/q_m$, then eqn. (10) becomes

$$E = R\left\{ \frac{2/T_i^3 + \left[\dfrac{\alpha q_i \gamma}{\Phi(\Delta H_0 - \Delta H_i) T_m^2} \right]}{(1/T_i^4) - (3\alpha\gamma/T_i^2 T_m^2) + (2\alpha^2\gamma^2/T_m^4)} \right\} \tag{11}$$

Equations (10) or (11) can be used to calculate the activation energy of the reaction.

VERIFICATION AND APPLICATION OF THE THEOREM

To verify the applicability of the obtained theorem, DSC thermograms were recorded using a Dupont 2000 differential scanning calorimeter. The samples tested were cyclotrimethylene trinitramine (RDX), cyclotetramethylene tetranitramine (HMX), pentaerythritol tetranitrate (PETN) and *N*-methyl-*N*-2,4,6-tetranitramine(tetryl). Published DSC and DTA data on the decomposition of these compounds were used for comparison. In the experiments, the sample weights were 2.0 ± 0.5 mg, except for HMX which was 1.0 ± 0.5 mg. Tests were performed at 10 and 6°C min^{-1}. Table 1 shows a comparison of the results obtained and the published results.

For RDX, the results obtained at the two different heating rates are almost the same. The calculated activation energy is shown in Table 1. Kishore [15] has discussed thermodecomposition in closed and open sys-

TABLE 1

Comparison of activation energy obtained by various methods

Materials	Method	Φ (°C min^{-1})	E (kcal mol^{-1})
RDX	Rogers and Smith [16] (closed pan)		26
	Kishore [15] (isothermal closed pan)		22 ± 2
	This study	10	20
HMX	Liu et al. [14] (DTA)		54.0
	Gibbs and Popolato [17] (DSC)		52.7 (liquid) 52.9 (vapor)
	This study	6	52.0
PETN	Liu et al. [14] (DTA)		31.3
	Gibbs and Popolato [17]		47.0 (liquid)
	This study	10	39.5
		6	42.0
Tetryl	Liu et al. [14] (DTA)		80.6
	This study	10	117.0
		6	122.0

tems. According to Kishore's report, the decomposition products have a catalytic effect on the decomposition of RDX, which decreases the activation energy. Our result for this decomposition is 20 kcal mol^{-1} which is within the range of Kishore's report (20 ± 2 kcal mol^{-1}).

For HMX, there is a superheating phenomenon at the higher heating rate of 10°C min^{-1}. At 6°C min^{-1}, the calculated activation energy is 52 kcal mol^{-1} which is very close to literature values [14,17].

For PETN, the results obtained by the method of this study at 10 and 6°C min^{-1} are 39.5 and 42.0 kcal mol^{-1} respectively. These results are within the range of other reports [14,17].

For tetryl, the results obtained from this study at the two heating rates are 117 and 122 kcal min^{-1}. There has been no other DSC study on tetryl. The only comparison is the DTA result of Liu et al. [14].

CONCLUSION

The area ratio concept and thermogram characteristics have been successfully combined in a direct method to calculate the activation energy of a decomposition reaction from a single DSC curve. The results determined by the present method are in fair agreement with literature reports but the procedure is much simpler.

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