

## Determination of kinetic parameters for decomposition reaction from a single DTA curve

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(Received 2 January 1991)

### Abstract

Relationships were derived for determining the three kinetic parameters of a general  $n$ th-order decomposition reaction from a single DTA curve. Doyle's approximation for the integral of the Arrhenius exponential function was used. The derivation was divided into three categories, for  $n > 1$ ,  $n = 1$ , and  $n < 1$ . Kissinger's semiempirical equation was employed to estimate the reaction order. The obtained relationships are fairly simple and the calculated results agree well with literature data. In particular, for  $n < 1$ , the calculation is straightforward without any iteration.

### INTRODUCTION

Differential thermal analysis (DTA) has been widely applied in studies of reaction kinetics and thermal properties. Kissinger [1] proposed a semidirect procedure to determine the activation energy  $E$ . Applying Kissinger's method, however, several DTA curves with different heating rates are required. In some papers [2,3] it was reported that the activation energy obtained by Kissinger's method is lower than that determined by other methods. Borham and Olson [2] also pointed out that Kissinger's method of calculating the reaction order produced a good result when applied to the exothermic DTA curve. Harris [4] reported that the activation energy of the cyclotetramethylene tetranitramine (HMX) decomposition reaction did not obey Kissinger's relationship.

Yang and Steinberg [5,6] proposed a model for determining the three kinetic parameters from a single DTA curve for a general  $n$ th-order reaction. Liu et al. [7] modified Yang and Steinberg's model and obtained a fairly convenient one. However, both the methods of Yang and Steinberg and of Liu et al. are still complicated and have to be solved by a trial and error approach. Blečić et al. [8] introduced the least squares method to calculate the kinetic parameters with a single DTA curve. However, the validity of this method is limited to values of  $E/RT$  less than unity.

For a general  $n$ th-order homogeneous decomposition reaction, the rate equation is always described as  $r = k(1 - x)^n$ . Whenever the rate equation is integrated, it is better to divide the discussion of kinetics into three categories, i.e.  $n < 1$ ,  $n = 1$  and  $n > 1$ . Nevertheless, both Yang and Steinberg [6] and Liu et al. [7] discussed only two categories ( $n = 1$  and  $n \neq 1$ ). Accordingly, the aim of this paper is to propose a simpler and more convenient method for rapidly calculating the kinetic parameters from a single DTA curve. A complete discussion for all three cases is presented.

## THEORETICAL CONSIDERATIONS

Most decomposition reactions of a solid to solid and/or gases can be described by a general rate equation

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

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. In a DTA curve, the temperature deviation  $\Delta T$  from that of a reference material could be approximated as being proportional to the rate of reaction

$$\Delta T = \beta(dx/dt) \quad (2)$$

where  $\beta$  is a proportionality constant. If  $T_0$  is the starting temperature and  $\phi$  is the constant heating rate, the temperature of the sample under test is given by the expression

$$T = T_0 + \phi t \quad (3)$$

Substituting eqn. (3) into eqn. (1), then integrating

$$\int_0^x \frac{dx}{(1 - x)^n} = \int_{T_0}^T \frac{A}{\phi} e^{-E/RT} dT \quad (4)$$

If  $n \neq 1$ , then

$$\frac{1}{n-1} \left[ \frac{1}{(1-x)^n} - 1 \right] = \frac{A}{\phi} \int_0^T e^{-E/RT} dT \quad (5)$$

The integral of the right-hand side of eqn. (5) can be expressed as an infinite series in terms of  $E/RT$ . This series is convergent only when  $E/RT$  is less than unity. Blečić et al. [8] developed their method with this assumption. For some cases of thermal analysis, however, the term  $E/RT$  is greater

than unity. Doyle [9] proposed the following simple relationship as a good approximation:

$$\frac{1}{n-1} \left[ \frac{1}{(1-x)^{n-1}} - 1 \right] \approx \frac{ART^2}{\phi E} e^{-E/RT} \quad (6)$$

Combining eqns. (1) and (6), we obtain

$$\Delta T = \beta A e^{-E/RT} \left[ \frac{ART^2}{\phi E} e^{-E/RT} (n-1) + 1 \right]^{n/(1-n)} \quad (7)$$

Although other assumptions were made by Yang and Steinberg [5,6] and by Liu et al. [7], the resulting equation is similar to eqn. (7). By using the above equation for calculating the kinetic parameters with a single DTA curve, both Yang and Steinberg [5,6] and Liu et al. [7] assumed  $\Delta T = 0$  at the end time  $t_e$ . Unfortunately, the value in square brackets of eqn. (7) is always greater than unity whenever  $n > 1$ . Therefore it is better to discuss the derivation in terms of three categories, i.e.  $n < 1$ ,  $n > 1$ , and  $n = 1$ .

(i) For  $n < 1$

In this category,  $\Delta T = 0$  at time  $t_e$  (or at the final temperature  $T_e$ ). The term in square brackets in eqn. (7) should be zero. After rearrangement, we obtain

$$A = \frac{\phi E}{(1-n)RT_e^2} e^{E/RT_e} \quad (8)$$

For the peak temperature  $T_m$ , eqn. (7) is differentiated with respect to  $T$  and the derivative is set as zero. It follows that

$$\begin{aligned} & \frac{E}{RT_m^2} e^u \left[ \frac{ART_m^2}{\phi E} e^u (n-1) + 1 \right]^{n/(1-n)} \\ & + e^u \left( \frac{n}{1-n} \right) \left[ \frac{ART_m^2}{\phi E} e^u (n-1) + 1 \right]^{1/(n-1)} \left[ \frac{AR}{\phi E} (n-1) \left( 2T_m + \frac{E}{R} \right) e^u \right] = 0 \end{aligned} \quad (9)$$

where  $u = -E/RT_m$ . By substituting eqn. (8) into eqn. (9), we obtain

$$\begin{aligned} \frac{1-n}{n} &= \frac{R}{E} \left( 2T_m + \frac{E}{R} \right) \frac{T_m^2}{T_e^2} \exp \left[ -\frac{E}{R} \left( \frac{T_e - T_m}{T_e T_m} \right) \right] \\ & \times \left\{ \frac{-T_m^2}{T_e^2} \exp \left[ -\frac{E}{R} \left( \frac{T_e - T_m}{T_e T_m} \right) \right] + 1 \right\}^{-1} \end{aligned} \quad (10)$$

For most decomposition reactions  $E/RT \gg 1$ , and it is reasonable to assume that  $(2T_m + E/R) \approx E/R$ . Equation (10) therefore could be approximated as

$$\frac{1-n}{n} \cong \frac{T_m^2}{T_e^2} \exp\left[-\frac{E}{R}\left(\frac{T_e - T_m}{T_e T_m}\right)\right] \left\{ -\frac{T_m^2}{T_e^2} \exp\left[-\frac{E}{R}\left(\frac{T_e - T_m}{T_e T_m}\right)\right] + 1 \right\}^{-1} \quad (11)$$

Furthermore, eqn. (11) can be simplified to

$$1-n = \frac{T_m^2}{T_e^2} \exp\left[-\frac{E}{R}\left(\frac{T_e - T_m}{T_e T_m}\right)\right] \quad (12)$$

Taking logarithms on both sides of eqn. (12), we obtain

$$\ln(1-n) \frac{T_e^2}{T_m^2} = -\frac{E}{R}\left(\frac{T_e - T_m}{T_e T_m}\right) \quad (13)$$

Beside eqns. (8) and (13), there is still one more equation required to determine the three kinetic parameters ( $n$ ,  $A$  and  $E$ ). Both Yang and Steinberg [6] and Liu et al. [7] employed the inflection temperature  $T_i$  at which the second derivative of eqn. (7) is set to zero. However, the second derivative of eqn. (7) is complicated and this approach is tedious. Kissinger [1] reported a semiempirical equation to estimate the reaction order with a "shape index"  $S$  which is the absolute value of the ratio of the slopes of the tangent at the inflection point on the right-hand side of the peak to that on the left-hand side. Both Borham and Olson [2] and Živković et al. [3] reported that the Kissinger method produced a good result for determining the reaction order:

$$n = 1.26 S^{1/2} \quad (14)$$

Equations (8), (13) and (14) can now be solved simultaneously without much difficulty and all three kinetic parameters are determined.

(ii) For  $n > 1$

In this category,  $\Delta T \neq 0$ , and eqn. (9) is useless. However, the mathematical characteristics, such as maximum and inflection points, of a curve would be useful. As  $n > 1$ , eqn. (10) can be simplified as follows:

$$A = \frac{\phi E}{RT_m^2} e^{E/RT_m} \quad (15)$$

For the inflection points of a DTA curve, the second derivative of eqn. (7) is taken and set to zero:

$$\left(\frac{E}{RT_i^2}\right)^2 - \frac{3nAE}{\phi RT_i^2} e^{-E/RT_i} \alpha_i + \frac{n(2n-1)}{\phi} A^2 e^{-2E/RT_i} \alpha_i^2 = 0 \quad (16)$$

where

$$\alpha_i = \left[ \frac{ART_i^2}{\phi E} e^{-E/RT_i} (n-1) + 1 \right]^{-1} \quad (17)$$

Generally, there are two inflection points on a DTA curve. In other words, there are two equations. We can determine the kinetic parameters ( $n$ ,  $A$  and  $E$ ) by solving these two equations with eqn. (15) simultaneously. Equation (16) is a non-linear algebraic equation and should be solved by an iterative method. Krug [11] extended Kissinger's method for the calculation of  $n$  for  $1 < n < 2$ .

$$n = \sqrt{\frac{S - 0.45}{0.18}} \quad (18)$$

Equation (18) can replace a complicated equation, eqn. (16), at one of two inflection temperatures. Accordingly, all three kinetic parameters are determined without too much difficulty by simultaneously solving eqns. (15), (16) and (18).

(iii) For  $n = 1$

Equation (4) can be integrated simply and the results are substituted into eqn. (2) to yield the following equation:

$$\Delta T = \beta A \exp\left(\frac{-E}{RT} - \frac{ART^2}{\phi E} e^{-E/RT}\right) \quad (19)$$

At the peak temperature,  $d(\Delta T)/dT = 0$ , we obtain

$$\frac{E}{RT_m^2} = \frac{AR}{\phi E} \left(2T_m + \frac{E}{R}\right) e^{-E/RT_m} \quad (20)$$

Normally  $E/RT$  is much larger than unity. It is reasonable to assume that  $E/R \gg 2T_m$ . Equation (20) is then simplified to eqn. (15), which is the same as one derived by Murray and White [12].

At the inflection temperature, the following equation is shown by setting  $d^2(\Delta T)/dt^2 = 0$

$$\frac{E}{RT_i^2} \left( \frac{E}{RT_i^2} - \frac{3A}{\phi} e^{-E/RT_i} - \frac{2}{T_i} \right) = -\frac{A^2}{\phi^2} e^{-2E/RT_i} \quad (21)$$

The above equation is the same as one which Yang and Steinberg [5]

derived. By solving eqns. (15) and (21) with the characteristic temperatures of a DTA curve,  $E$  and  $A$  can be calculated.

#### VERIFICATION AND APPLICATION OF THE THEOREM

The general theorem has been derived for determining the kinetic parameters of a decomposition reaction from a single DTA curve as above. Except for  $n < 1$ , the related equations are non-linear and have to be solved simultaneously. As reported by both Yang and Steinberg [6] and Liu et al. [7], a trial and error method should be employed. For solving a set of non-linear equations with an iterative approach, however, a good first conjecture is important. In this paper, a shape index, defined by Kissinger, of a DTA curve is suggested to estimate the reaction order as the first conjecture. If the shape index is between 0 and 0.63, eqn. (14) is used and  $n < 1$  is found. If  $S > 0.63$ , eqn. (18) is employed and  $n > 1$  obtained. The calculation is then appreciably simplified and the related equation converges quickly.

To demonstrate the applicabilities of the obtained theorem, published DTA thermograms on the decomposition of both inorganic and organic compounds have been employed in conjunction with the derived equations. The calculated kinetic parameters are compared with literature data. As for the above derivation, the verification is divided into three categories.

##### (i) For $n < 1$

Table 1 lists the comparison of the reported kinetic parameters obtained from previous methods and the present method. It is found that the activation energy calculated by this method is in fair agreement with that from experiment or obtained by other methods. Živković et al. [3] studied the kinetics of the thermal decomposition of copper basic carbonate by DTA with different heating rates and by thermogravimetric analysis (TG). They reported that the activation energy of the reaction is  $14.82 \text{ kcal mol}^{-1}$  by the Kissinger method with DTA curves and  $17.08 \text{ kcal mol}^{-1}$  by TG. The value estimated by the Kissinger method is a little lower. Using eqn. (14), reaction orders of 0.73 and 0.82 were obtained for the given DTA curves with heating rates of  $5^\circ\text{C min}^{-1}$  and  $10^\circ\text{C min}^{-1}$ , respectively. Equations (8) and (13) were then employed to determine the activation energy and pre-exponential factor. The activation energy estimated by this method is much closer to that obtained by TG.

Yang and Steinberg [6] studied the rates of decomposition of calcitic limestone by isothermal TG and non-isothermal DTA measurements. They reported that the activation energy of limestone decomposition is about  $44 \text{ kcal mol}^{-1}$  from either TG or DTA data. Based on the DTA curves reported by Yang and Steinberg [6], the kinetic parameters of limestone decomposi-

TABLE 1

Comparison of kinetic parameters obtained by various methods for  $n < 1$ 

Reactant	Calculation method	$\phi$ ( $^{\circ}\text{C min}^{-1}$ )	$n$	$E$ (kcal mol $^{-1}$ )	$A$
Basic copper carbonate	TG [3]			17.08	
	Kissinger's method [3]	5	0.73	14.82	$1.2 \times 10^5$
	This work	10	0.82	18.74	$1.5 \times 10^5$
			0.55	18.43	$1.6 \times 10^6$
			0.55	44.0	$1.9 \times 10^6$
Limestone	Isothermal TG [6]	6	0.55	44.0	$1.2 \times 10^6$
	Yang and Steinberg [6]	10	0.57	43.0	$1.9 \times 10^6$
		15	0.56	44.0	$2.8 \times 10^6$
	This work	6	0.56	45.0	$2.2 \times 10^6$
		10	0.58	44.4	$2.2 \times 10^6$
RDX <sup>a</sup>		15	0.59	43.6	$1.5 \times 10^6$
	Reich [13]	6	0.8	80.0	
	Kissinger's method [4]			34.68	$8.3 \times 10^{12}$
	Liu et al. [7]		0.65	32.5	$4.1 \times 10^{11}$
	This work	6	0.57	35.3	$3.6 \times 10^{12}$
PETN <sup>b</sup>	Reich [14]	6	$1.0 \pm 0.1$	$59.0 \pm 3$	$2.5 \times 10^{13}$
	Kissinger's method [4]			33.0	$1.8 \times 10^6$
	Liu et al. [7]		0.89	31.3	$3.1 \times 10^6$
	This work	6	0.95	38.3	

<sup>a</sup> RDX, cyclotrimethylenetrinitramine. <sup>b</sup> PETN, pentaerythritol tetranitrate.

tion are obtained by means of eqns. (8), (13) and (14). The activation energy obtained by this method is in fair agreement with that calculated using the relationships derived by Yang and Steinberg.

Reich [13,14] proposed an areal method for estimating overall values of  $E$  and  $n$  for polymer degradation, and applied it to the thermal decomposition of energetic organic compounds. He reported that the activation energies of cyclotrimethylenetrinitramine (RDX) and pentaerythritol tetranitrate (PETN) are 80 kcal mol<sup>-1</sup> and 59 kcal mol<sup>-1</sup>, respectively. Harris [4] employed the Kissinger method in determining activation energies of 34.68 and 33.0 kcal mol<sup>-1</sup> for RDX and PETN, respectively. Liu et al. [7] reported an activation energy obtained by their method that was even lower than those found by the Kissinger method. In this study, the DTA curves of Reich are used in conjunction with eqns. (8), (13) and (14) to calculate the kinetic parameters. The results are included in Table 1, along with the values calculated by other methods. Apparently, the activation energy obtained by the Reich method is too high. It should be noted that the kinetic parameters determined by the present method are comparable with the experimental data for both inorganic and organic compounds.

(ii) For  $n = 1$

The kinetics of decomposition of benzenediazonium chloride in aqueous solution were studied isothermally by Crossley et al. [15] and the non-isothermal DTA curve was measured and analysed by Borchardt and Daniels [10]. Crossley et al. [15] found the reaction to be first order with an activation energy of 27.2 kcal mol<sup>-1</sup>. The shape index obtained from the DTA curve presented by Borchardt and Daniels is 0.63. The reaction order is then calculated to be unity using either eqn. (14) or eqn. (18). The kinetic parameters obtained using eqns. (15) and (21) are listed in Table 2, along with those calculated by other methods. From the comparison, it is seen that

TABLE 2

Comparison of kinetic parameters obtained by various methods for  $n=1$  and  $n > 1$

Reactant	Calculation method	$\phi$ ( $^{\circ}\text{C min}^{-1}$ )	$n$	$E$ (kcal mol <sup>-1</sup> )	$A$
For $n = 1$					
Benzenediazonium chloride in solution	Crossley et al. [15]	(Isothermal)	1	27.2	$1.0 \times 10^{15.2}$
	Borchardt and Daniel [10]	1	1	28.3	$1.0 \times 10^{16.3}$
	Yang and Steinberg [6]		0.9	30.0	$1.0 \times 10^{17.4}$
	This work	1	1	26.1	$1.0 \times 10^{14.7}$
For $n > 1$					
Cellulose nitrate	Reich [13]	6	4.6	180.0	
	This work	6	2.0	117.0	$8.1 \times 10^{51}$



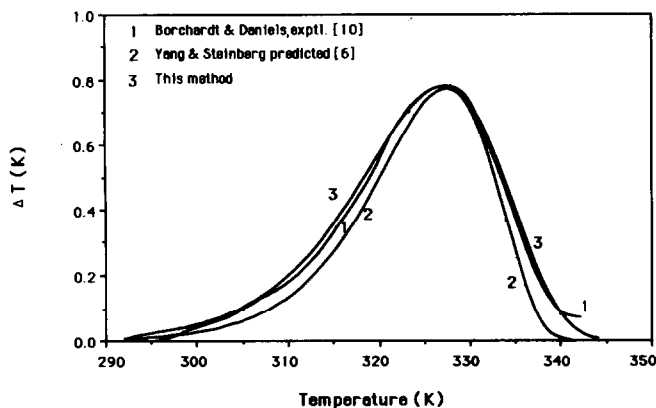


Fig. 1. Calculated and experimental DTA curves for the decomposition of benzenediazonium chloride.

the method of Yang and Steinberg [6] gives slightly higher values for  $E$  and  $A$ . The values obtained by this method and by the method of Borchardt and Daniels are equally close to those reported by Crossley et al., although the deviations have the opposite sign.

Yang and Steinberg [6] predicted the DTA curve from known kinetic parameters and explained the deviation by the thermal effect. In fact, there is a proportionality constant  $\beta$  in eqn. (7) or (19) which can be used to calculate  $\Delta T$ . Yang and Steinberg assumed  $\beta$  to approximate to the heat of reaction divided by the total heat capacity of the sample mass. This assumption might cause a deviation of the calculated  $\Delta T$  from the experimental value. Owing to the uncertainty,  $\beta$  is back-calculated from  $\Delta T$  at the peak temperature of the given DTA curve and the known kinetic parameters using eqn. (7) or (19). In Fig. 1, the DTA curves calculated from eqn. (19) and by Yang and Steinberg [6] are shown along with the experimental curve reported by Borchardt and Daniels [10]. It is found that the result by the present method is better than that of Yang and Steinberg.

(iii) For  $n > 1$

Reich [13] studied the decomposition of cellulose nitrate (CN) with a nitrogen content of 12.2% by DTA with a heating rate of  $6^\circ\text{C min}^{-1}$ , and calculated the activation energy from the DTA result by his method. According to the DTA curve Reich reported, the shape index was found to be 1.17. Using eqn. (18), the reaction order was found to be 2.0. The kinetic parameters were then solved using eqns. (15) and (16). The results are listed in Table 2, along with those calculated by Reich. The activation energy and the reaction order obtained by this method are much lower than those reported by Reich. As aforementioned, the activation energy determined by Reich's method is too high.

## CONCLUSION

The shape index obtained from a single DTA curve is employed to estimate the reaction order. For  $n < 1$ , eqns. (8) and (13) can be used to calculate  $E$  and  $A$  quickly without any iteration. For  $n = 1$ , eqns. (15) and (21) can be used and for  $n > 1$ , eqns. (15) and (16) are employed. The kinetic parameters for a decomposition reaction determined by the present method are in fair agreement with literature data.

## REFERENCES

- 1 H.E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
- 2 B.M. Borham and F.A. Olson, *Thermochim. Acta*, 6 (1973) 345.
- 3 Ž.D. Živković, D.F. Bogosavljević and V.D. Zlatković, *Thermochim. Acta*, 18 (1977) 310.
- 4 J. Harris, *Thermochim. Acta*, 14 (1976) 183.
- 5 R.T. Yang and M. Steinberg, *J. Phys. Chem.*, 80 (1976) 965.
- 6 R.T. Yang and M. Steinberg, *Anal. Chem.*, 49 (1977) 998.
- 7 Z.R. Liu, C.M. Yin, Ch.Y. Wu and M.N. Chang, *Propellants, Explos. Pyrotech.*, 11 (1986) 10.
- 8 D. Blečić, Ž.D. Živković and M. Martinović, *Thermochim. Acta*, 60 (1983) 61.
- 9 C.D. Doyle, *J. Appl. Polym. Sci.*, 15 (1961) 285.
- 10 H.J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, 79 (1957) 41.
- 11 D. Krug, *Thermochim. Acta*, 10 (1974) 217.
- 12 P. Murray and J. White, *Trans. Br. Ceram. Soc.*, 54 (1955) 204.
- 13 L. Reich, *Thermochim. Acta*, 5 (1973) 433.
- 14 L. Reich, *Thermochim. Acta*, 8 (1974) 399.
- 15 M.L. Crossley, R.H. Kienle and C.H. Benbrook, *J. Am. Chem. Soc.*, 62 (1940) 1400.