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## Calculation of kinetic parameters from DTA curves using the characteristic temperature

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### Abstract

Kinetic parameter equations were derived for estimating a general  $n$ th-order decomposition reaction from a single DTA curve. These categories, for  $n < 1$ ,  $n = 1$ , and  $n \neq 1$ , were derived. Three kinetic parameters, the activation energy  $E$ , reaction order  $n$ , and pre-exponential factor  $A$ , can be expressed as functions of the characteristic temperatures  $T_0$ ,  $T_{i1}$ ,  $T_m$ , and  $T_e$  which are the decomposition starting point, first inflection point, peak maximum point and end point on the DTA curve, respectively. All of the kinetic parameter calculations are straightforward without any iteration.

*Keywords:* Activation energy; Decomposition; DTA; Kinetics

### List of symbols

$A$	pre-exponential factor of the Arrhenius equation
$B$	factor in Eq. (7)
$E$	activation energy
$n$	reaction order
$R$	gas constant
$T$	absolute temperature
$T_{i1}, T_{i2}$	inflection temperature
$T_e$	end decomposition temperature of DTA curve
$T_m$	peak temperature of DTA curve
$T_0$	starting decomposition temperature of DTA curve

$t$	time
$x$	fraction of material reacted

### Greek letters

$\alpha$	factor in Eq. (7)
$\beta$	proportionality constant
$\Delta$	difference
$\phi$	constant heating rate

## 1. Introduction

The use of differential thermal analysis (DTA) to evaluate kinetic parameters has been widely studied by many investigators. Kissinger [1] proposed a semi-empirical formula to calculate the reaction order and to evaluate the activation energy using the values of various heating rates and maximum temperature of DTA curves. This semi-empirical equation can be applied for  $n < 1$  only. Huang and co-workers [2,3] also applied the Kissinger formula and another modified Kissinger formula to estimate reaction order for  $n < 1$  and  $n > 1$  in the three categories,  $n < 1$ ,  $n = 1$ , and  $n > 1$ , and applied their simplified equations to calculate activation energy  $E$  and pre-exponential factor  $A$ . Yang and Steinberg [4,5] used the peak temperature  $T_m$  of the first derivative and two inflection temperatures  $T_{i1}$  and  $T_{i2}$  of the second derivative of the DTA curve to solve reaction order as  $n \neq 1$ . The calculated results are unreasonable for the values of  $T_{i1}$  and  $T_{i2}$  since they represent two different roots solved from the same equation. They are not totally independent. Liu et al. [6] modified the Yang and Steinberg model and used  $T_m$ ,  $T_{i1}$  and the starting and ending temperatures  $T_o$  and  $T_e$  to obtain a fairly convenient model. However, all of these methods of Huang et al., Yang and Steinberg, and Liu et al. are still very complicated and have to be solved by a trial and error approach to obtain the values of  $E$  and  $A$ .

In this investigation, a very brief and accurate relationship will be derived from a single DTA curve to evaluate the decomposition kinetic parameters,  $n$ ,  $E$ , and  $A$ , in three categories,  $n < 1$ ,  $n = 1$ , and  $n \neq 1$ . These methods represent a more convenient method for the rapid calculation of the kinetic parameters from a single DTA curve than any of the previous methods. A detail discussion of this method is presented here.

## 2. Theoretical

In general, the expression of solid decomposition reactions of  $n$ th order can be described as

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

where  $dx/dt$  is the rate,  $x$  is the fraction of the material reacted,  $A$  is the pre-exponential factor of the Arrhenius equation,  $n$  is the reaction order,  $E$  is the activation energy,  $R$  is the gas constant and  $T$  is the absolute temperature. On a DTA curve, the temperature deviation from a set horizontal baseline can be assumed to be proportional to the reaction rate of material decomposition

$$\Delta T = \beta \frac{dx}{dt} \quad (2)$$

where  $\beta$  is a proportional constant. If  $T_0$  is the starting temperature and  $\phi$  is the constant heating rate, we can express the temperature of reaction as

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

Combining Eqs. (1) and (3), and then integrating

$$\int_0^x \frac{dx}{(1-x)^n} = A \int_0^t e^{-E/R(T_0 + \phi t)} dt \quad (4)$$

Integration of the right hand side of Eq. (4) can be approximated as

$$\begin{aligned} e^{-E/R(T_0 + \phi t)} &= e^{-(E/RT_0)[1/(1 + \phi t/T_0)]} \\ &= e^{-(E/RT_0)[1 - (\phi t/T_0) + (\phi t/T_0)^2 - \dots]} \\ &\approx e^{-(E/RT_0)[1 - (\phi t/T_0)]} \end{aligned} \quad (5)$$

Substituting Eq. (5) and Eq. (4) and integrating, gives

$$[1/(n-1)][1/[(1-x)^{n-1}] - 1] = (ART_0^2/\phi E)e^{-E/RT_0}[e^{(\phi E/RT_0^2)t} - 1] \quad (6)$$

Let

$$\alpha = \frac{\phi E}{RT_0^2} \quad \text{and} \quad B = \frac{A(n-1)}{\alpha e^{E/RT_0}}$$

and Eq. (6) can be expressed as

$$(1-x) = [B(e^{\alpha t} - 1) + 1]^{1/(1-n)} \quad (7)$$

Combining Eqs. (1), (2), (3), and (7), the temperature deviation can be expressed as

$$\Delta T = \beta A e^{-E/RT_0} e^{\alpha t} [B e^{\alpha t} + (1-B)]^{n/(1-n)} \quad (8)$$

At  $T = T_m$  and  $t = t_m$ , the deflection of the DTA curve is maximal and  $d\Delta T/dt = 0$ ; thus

$$\frac{d\Delta T}{dt} = \alpha \Delta T + \frac{nB\alpha e^{\alpha t}}{(1-n)[B e^{\alpha t} + (1-B)]} \Delta T = 0 \quad (9)$$

From Eq. (9), we can obtain the relationship

$$\frac{B}{1-B} e^{\alpha t_m} = (n-1) \quad (10)$$

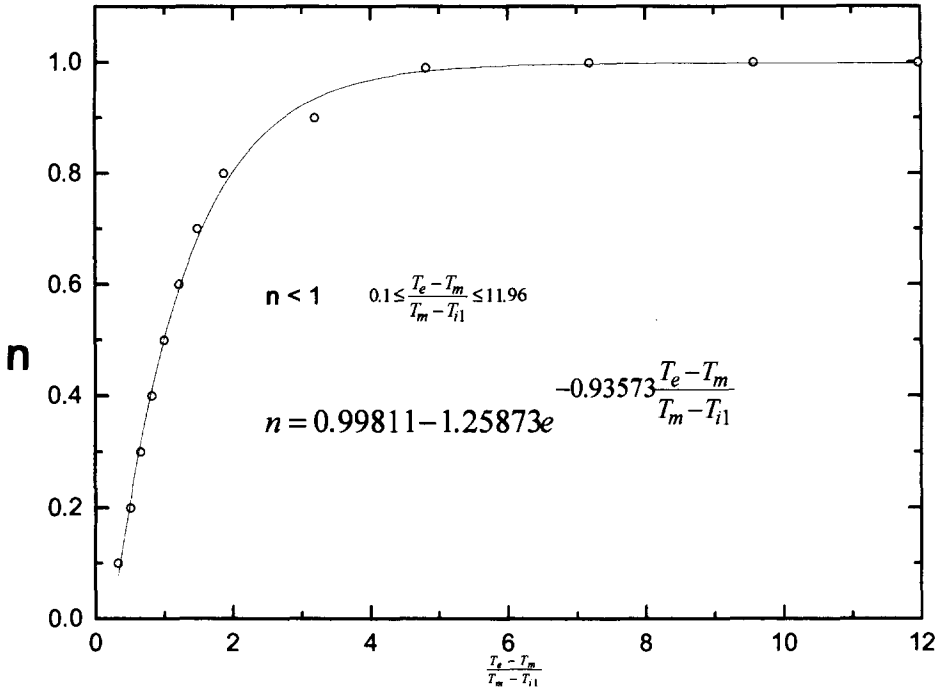


Fig. 1. Relationships of  $n$  and  $(T_e - T_m)/(T_m - T_{i1})$  for  $n < 1$  from eqn (16).

There are two points of inflection on the DTA curve: at  $T_{i1}$  and  $T_{i2}$  at time  $t_{i1}$  and  $t_{i2}$ . These two points can be found by setting the second derivative of the temperature deviation equal to zero, i.e.  $d^2\Delta T/dt^2 = 0$ . Then we can obtain the next two equations

$$\frac{B}{1 - B} e^{\alpha t_{i1}} = \frac{(n - 1)[2 + n - \sqrt{n(n + 4)}]}{2} \tag{11}$$

and

$$\frac{B}{1 - B} e^{\alpha t_{i2}} = \frac{(n - 1)[2 + n + \sqrt{n(n + 4)}]}{2} \tag{12}$$

At the final decomposition time  $t_e$  and temperature  $T_e$ , the temperature deviation  $\Delta T$  from the baseline is set to zero. Therefore, from Eq. (8) we can obtain the equation at the end point as

$$\frac{B}{1 - B} e^{\alpha t_e} = -1 \tag{13}$$

Dividing Eq. (13) by Eq. (10) yields

$$e^{\alpha(t_e - t_m)} = \frac{1}{1 - n} \tag{14}$$

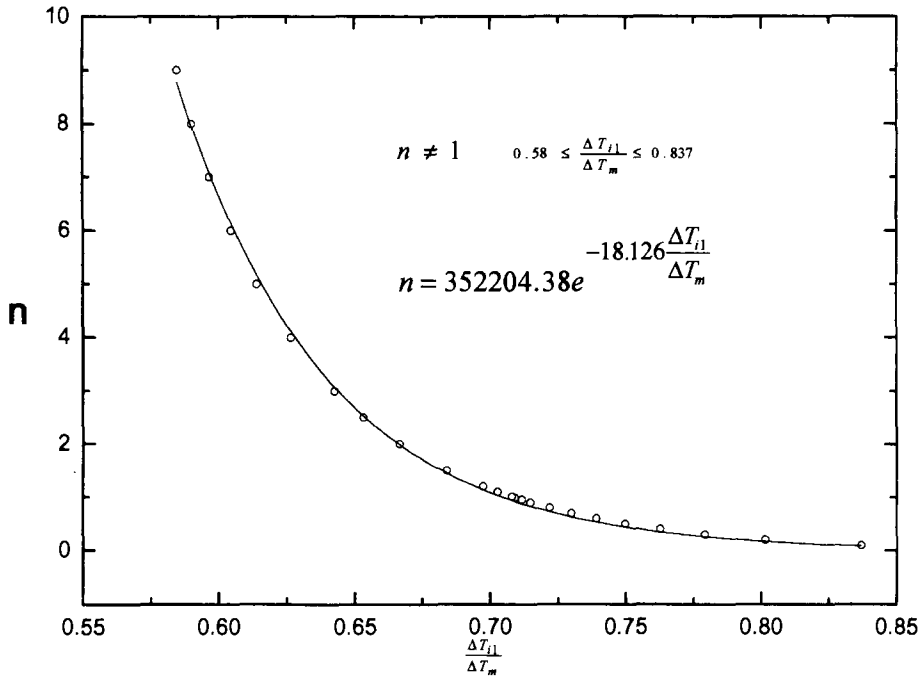


Fig. 2. Relationships of  $n$  and  $(\Delta T_{i1})/(\Delta T_m)$  for  $n \neq 1$  from eqn (20).

Then, dividing Eq. (10) by Eq. (11) yields

$$e^{\alpha(t_m - t_{i1})} = \frac{2}{2 + n - \sqrt{n(n+4)}} \quad (15)$$

Taking the natural logarithm on both sides of Eqs. (14) and (15) and dividing the first term by the second term and then combining with Eqs. (3) gives

$$\frac{T_c - T_m}{T_m - T_{i1}} = \frac{\ln(1 - n)}{\ln\left[\frac{2 + n - \sqrt{n(n+4)}}{2}\right]} \quad (16)$$

Eq. (16) is the same as that derived by Liu et al. [6]. From this equation, we see that the values of  $n$  must be less than unity. The value of the reaction order is a function of the measurable characteristic temperatures  $T_c$ ,  $T_m$ , and  $T_{i1}$ . However, this equation is not convenient for estimating the value of  $n$  which has to be solved by a trial and error approach. In order to obtain a convenient equation for the reaction order calculation, the values of  $n$  versus  $(T_c - T_m)/(T_m - T_{i1})$  are plotted in Fig. 1. Then, using curve fitting, we can express  $n$  as a function of the characteristic temperatures

$$n = 0.99811 - 1.25873e^{-0.93573(T_c - T_m)/(T_m - T_{i1})} \quad (17)$$

Eq. (17) is only used in the range of  $n < 1$ , or  $0.1 \leq (T_c - T_m)/(T_m - T_{i1}) \leq 11.96$ . Using this equation, we can estimate the reaction order of decomposition very

conveniently and quickly. After obtaining the value of  $n$ , the values of  $E$  and  $A$  can be evaluated. From Eqs. (3) and (14), we obtain

$$E = \frac{RT_0^2}{T_m - T_e} \ln(1 - n) \quad (18)$$

From Eqs. (3) and (10), the value of the pre-exponential factor of the Arrhenius equation can be expressed as

$$A = \frac{(E\phi/RT_0^2)e^{E/RT_0}}{e^{[E(T_m - T_0)]/RT_0^2} + (n - 1)} \quad (19)$$

Eqs. (16)–(18) are valid for  $n < 1$  only. When this does not hold, these equations are useless. Liu et al. suggested combining Eqs. (8), (10) and (11) to give

$$\frac{\Delta T_{i1}}{\Delta T_m} = \left[ \frac{2 + n - \sqrt{n(n+4)}}{2} \right] \left[ \frac{(n-1)[2 + n - \sqrt{n(n+4)}] + 2}{2n} \right]^{n/(1-n)} \quad (20)$$

Eq. (20) is more complicated than Eq. (16). Using this equation to evaluate the values of  $n$  is arduous. In order to solve this problem, we plot the calculated values of  $n$  versus  $\Delta T_{i1}/\Delta T_m$  from Eq. (20) as shown in Fig. 2. Again, after using the method of curve fitting, the reaction order  $n$  can be expressed as a function of the characteristic temperatures in a very simply way

$$n = 352204.38e^{-18.126(\Delta T_{i1}/\Delta T_m)} \quad (21)$$

Eq. (21) is valid in the range of  $n \neq 1$  or  $0.58 \leq (\Delta T_{i1}/\Delta T_m) \leq 0.837$ . The values of  $\Delta T_{i1}$  and  $\Delta T_m$  are the distances of  $T_{i1}$  and  $T_m$  from the baseline to the curve respectively. The value of  $E$  in this category can be calculated by rearrangement of Eq. (15)

$$E = RT_0^2/(T_m - T_{i1}) \ln[(2 + n + \sqrt{n(n+4)})/2] \quad (22)$$

The values of the pre-exponential factor  $A$  in this category can be calculated using Eq. (19).

If the relationship between the characteristic temperatures,  $(T_e - T_m)/(T_m - T_{i1})$ , is greater than 11.96, the reaction order is equal to unity. Eq. (1) becomes

$$\frac{dx}{dt} = A(1 - x)e^{-E/RT} \quad (23)$$

The first derivative of Eq. (23) can be used to find  $T = T_m$  at time  $t = t_m$

$$\frac{d}{dt} \left( \frac{dx}{dt} \right) = \left[ \frac{\phi E}{RT^2} - A e^{-E/RT} \right]_{T=T_m} \frac{dx}{dt} = 0 \quad (24)$$

Thus, we can obtain for  $n = 1$

$$A = \frac{\phi E}{RT_m^2} e^{E/RT_m} \quad (25)$$

The second derivative of Eq. (23) can be used to obtain two inflection temperatures  $T_{i1}$  and  $T_{i2}$  at time  $t_{i1}$  and  $t_{i2}$  respectively. The result is

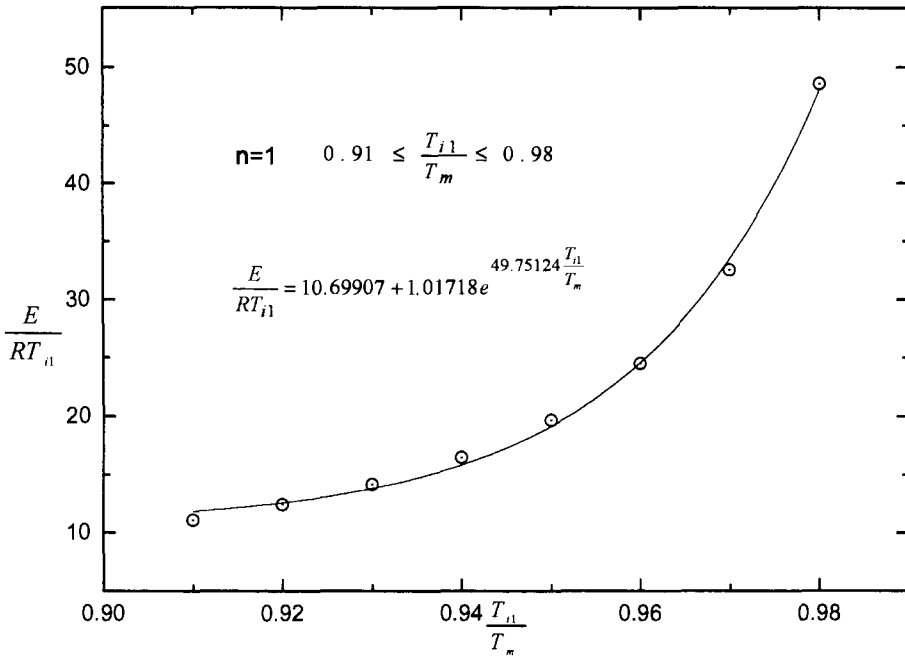


Fig. 3. Relationships of  $E/RT_{i1}$  and  $(T_{i1})/(T_m)$  for  $n = 1$  from eqn (29).

$$\frac{d^2}{dt^2} \left( \frac{dx}{dt} \right) = \left[ \left( \frac{\phi^2 E^2}{R^2 T^4} - \frac{2\phi^2 E}{RT^3} \right) - \frac{3\phi E}{RT^2} A e^{-E/RT} + (A e^{-E/RT})^2 \right] \frac{dx}{dt} = 0 \quad (26)$$

The solution of Eq. (26) can be obtained as two roots

$$A e^{-E/RT_{i1}} = \frac{\phi E}{RT_{i1}^2} \left[ \frac{3 - \sqrt{5 + 8 \frac{RT_{i1}}{E}}}{2} \right] \quad (27)$$

and

$$A e^{-E/RT_{i2}} = \frac{\phi E}{RT_{i2}^2} \left[ \frac{3 - \sqrt{5 + 8 \frac{RT_{i2}}{E}}}{2} \right] \quad (28)$$

Combining Eqs. (25) and (27) to eliminate  $A$ , we can calculate the activation energy from the following equation for  $n = 1$

$$E = \frac{T_m T_{i1} R}{T_m - T_{i1}} \left[ 2 \ln \frac{T_m}{T_{i1}} - \ln \left( 1.5 - \sqrt{1.25 + \frac{2RT_{i1}}{E}} \right) \right] \quad (29)$$

For high activation energy materials,  $E \gg 2RT_{i1}$ , the last term inside the square root can be neglected. Consequently, this equation can be simplified as

$$E \approx \frac{T_m T_{i1}}{T_m - T_{i1}} \left[ 1.9123 + 3.974 \ln \frac{T_m}{T_{i1}} \right] \quad (30)$$

for  $n = 1$ . When the activation energy is not very high, Eq. (29) should produce some truncation error if we neglect the last term inside the square root. In order to obtain an exact value of  $E$  from Eq. (29), we have to solve it by a tedious trial and error method. Therefore, the relationships between  $E/RT_{i1}$  and  $T_{i1}/T_m$  were calculated from Eq. (29) and plotted in Fig. 3. After curve fitting, their correlation can be expressed as

$$E/RT_{i1} = 13.54925 + 3.58857 \times 10^{-19} e^{47.05882(T_{i1}/T_m)} \quad (31)$$

for  $n = 1$ . Eq. (31) can also be expressed as

$$E = T_{i1} [26.92236 + 7.1305 \times 10^{-19} e^{47.05882(T_{i1}/T_m)}] \quad (32)$$

for  $n = 1$ . From Eq. (32), the first-order reaction activation energy can be calculated very easily. This equation is only valid in the range  $0.90 \leq (T_{i1}/T_m) \leq 0.98$ .

### 3. Verification and application of the theorem

Yang and Steinberg [5] expressed the reaction order  $n$  as a function of  $T_e$ ,  $T_m$  and  $T_{i1}$  for  $n < 1$  and as a function of  $T_{i1}$ ,  $T_{i2}$  and  $T_m$  for  $n \neq 1$ . The calculation cannot always provide a convergent solution for  $n \neq 1$  due to the variables  $T_{i1}$  and  $T_{i2}$  which are solved using the same equation. Liu et al. [6] modified the Yang and Steinberg model and obtained a fairly convenient one. However, it is difficult to obtain a solution of the reaction order  $n$  from their complicated equations. Kissinger [1] proposed a shape index semi-empirical equation to calculate reaction order for  $n < 1$ . This equation is convenient for the estimation of reaction order. However, using Kissinger's model to estimate the activation energy requires various heating rates. Huang and co-workers [2,3] also used Kissinger's model to estimate the reaction order for  $n < 1$  and modified the Kissinger model to calculate the reaction order for  $1 < n < 2$ . There is no way to calculate reaction order for  $n > 2$ . Therefore, the above methods to calculate the kinetic parameters are still complicated and inconvenient. Even Huang and co-workers used the Kissinger model to estimate reaction order to avoid complicated iteration; the activation energy and pre-exponential factor calculations in their model still need to be solved by trial and error iterations. Comparing all of these models, the equations presented here are more effective and convenient than any of the other equations in the kinetic parameter calculations.

A brief, convenient theorem has been derived above in the three categories,  $n < 1$ ,  $n = 1$ , and  $n \neq 1$ , for calculating the kinetic parameters of a decomposition reaction from a single DTA curve. Knowing the characteristic temperatures of a DTA curve, the kinetic parameters  $n$ ,  $E$ , and  $A$  can be evaluated very quickly and accurately from the above derived equations. In order to demonstrate this derived theorem, DTA thermograms for the decomposition of energetic and other materials pub-



Table 1  
Comparison of kinetic parameters obtained by various methods ( $n = 1$ )

Yang and Steinberg [5]	$\phi/(^{\circ}\text{C min}^{-1})$	$E/(\text{kcal mol}^{-1})$	$A/\text{s}^{-1}$
Decomposition of benzenediazonium chloride, $T_m = 53.93^{\circ}\text{C}$ , $T_{i1} = 46.45^{\circ}\text{C}$			
Crossley et al. [7]	0	27.2	$1.0 \times 10^{15.2}$
Borchardt and Daniel [8]	1	28.3	$1.0 \times 10^{16.3}$
Huang et al. [2]	1	26.1	$1.0 \times 10^{14.7}$
This work	1	29.8 (Exact)	$1.0 \times 10^{17.3}$
	1	27.1 (Approx.)	$1.0 \times 10^{15.4}$
Decomposition of $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$ , $T_m = 1293^{\circ}\text{C}$ , $T_{i1} = 1221^{\circ}\text{C}$			
Value in literature [1]	10	71.16	$3.32 \times 10^7$
Yang and Steinberg [5]	10	72.00 (Approx.)	$3.25 \times 10^7$
	10	66.00 (Exact)	$4.11 \times 10^6$
This work	10	73.71 (Exact)	$4.88 \times 10^7$
	10	68.23 (Approx.)	$7.76 \times 10^6$
Dehydration of Goergia kaolinite, $T_m = 600^{\circ}\text{C}$ , $T_{i1} = 555^{\circ}\text{C}$			
Value in literature [1]	6	34.97	$1.29 \times 10^6$
Yang and Steinberg [5]	6	35.00	$1.23 \times 10^6$
This work	6	36.59 (Exact)	$3.49 \times 10^6$
	6	34.11 (Approx.)	$7.78 \times 10^5$
Dehydration of Eureka halloysite, $T_m = 533^{\circ}\text{C}$ , $T_{i1} = 496^{\circ}\text{C}$			
Value in literature [1]	6	35.85	$1.66 \times 10^7$
Yang and Steinberg [5]	6	36.00	$2.05 \times 10^7$
This work	6	37.94 (Exact)	$5.68 \times 10^7$
	6	35.18 (Approx.)	$9.41 \times 10^6$

lished by previous authors have been employed to calculate kinetic parameters. The calculated results are compared with literature data.

### 3.1. Case of $n = 1$

The kinetics of the first-order reactions can be solved analytically provided  $E$  and  $A$  are functions of  $T_{i1}$  and  $T_m$  only. These final relationships have been shown in Eqs. (32) and (25) respectively. In Eqs. (29), we see that the values of  $E$  have to be greater than  $2RT_{i1}$ , otherwise there is no solution in this equation. If  $E \gg 2RT_{i1}$ , then Eq. (29) can be simplified into Eq. (30). In that case, the activation energy is very high. The DTA curve must be very narrow and sharp, or  $T_{i1}$  is close to  $T_m$ .

Four first-order decomposition reactions were selected from the literature as shown in Table 1. The estimated  $E$  and  $A$  values are compared with those previously determined. The kinetics of decomposition of benzenediazonium chloride solution were studied isothermally by Crossley et al. [7] and the non-isothermal DTA curve was measured by Borchardt and Daniels [8]. The approximate solution of the activation energy  $E$  is very close to the experimental data of Crossley et al.,

i.e.  $E = 27.2 \text{ kcal mol}^{-1}$ . The exact solution gives slightly higher values and the method of Huang et al. gives slightly lower values of  $E$  and  $A$ .

Other first-order reactions are the decomposition of  $\text{CO}_2 + \text{C}$ , the dehydration of Georgia kaolinite, and the dehydration of Euraka halloysite. All of these kinetic parameters are obtained from Yang and Steinberg [4,5] and Kissinger [1]. The calculated  $E$  and  $A$  values for both the exact and approximate solutions are better than Yang and Steinberg's calculations and close to the experimental results. Yang and Steinberg used the calculated values of  $E$  and  $A$  to predict the rates of  $\text{CO}_2 + \text{C}$  reaction. Their predicted values are lower than the experimental data determined isothermally. This is because the temperatures measured ( $T_{i1}$  and  $T_m$ ) were the reference temperatures, and during the reaction the sample temperature was lower than the reference and the heating rate was also lower before the peak temperature. Consequently, lower  $T_{i1}$  and  $T_m$  values lead to lower estimated  $E$  and  $A$ . In this calculation, all the values of activation energy and pre-exponential factor are higher than the Yang and Steinberg predictions. The approximate solutions yield a lower value than the exact solutions and the Yang and Steinberg predictions neglect the last term inside the square root of Eq. (29). However, the approximate calculation of the present method is better than any of the other evaluations.

### 3.2. Case of $n \neq 1$

There are two categories for  $n \neq 1$ , i.e.  $n < 1$  and  $n > 1$ . The kinetic parameters  $n$ ,  $E$ , and  $A$  can be calculated using Eqs. (17), (18), and (19) in the category of  $n < 1$  or  $0.1 \leq (T_e - T_m)/(T_m - T_{i1}) \leq 11.96$ , and Eqs. (21), (22) and (19) in the category of  $n \neq 1$  or  $0.58 \leq (\Delta T_{i1}/\Delta T_m) \leq 0.837$ . Various kinetic parameter calculation methods have been reviewed and listed by Huang and co-workers [2,3]. The reaction order and activation energy calculated by this method is in fair agreement with those obtained from experiments or from other methods. Yang and Steinberg [5] studied the rates of decomposition of calcitic limestone by isothermal TG and non-isothermal DTA measurement. They reported that the values of reaction order  $n$  are between 0.55 and 0.57, and that the activation energy  $E$  is about  $44 \text{ kcal mol}^{-1}$ . The Huang calculated values of  $n$  are in the range 0.56–0.59, and the values of  $E$  are about  $43.6\text{--}45 \text{ kcal mol}^{-1}$ . In this calculation, we found that the values of  $n$  are between 0.51 and 0.60 for various heating rates. These results are very close to the previously calculated results of Yang and Steinberg and Huang and co-workers. However, the calculated values of the activation energy are in the range  $27.4\text{--}35.3 \text{ kcal mol}^{-1}$ . This result is lower than those of previous methods.

The kinetic parameters of energetic materials, i.e. TNT (trinitrotoluene), RDX (cyclotrimethylenetrinitramine), HMX (cyclotetramethylene tetranitramine), Tetryl, and PETN (pentaerythritol tetranitrate), were calculated and compared with the results of previous studies. All the experimental data are from Huang and Wu [3]. As shown in Table 2, all of these reactions are in the category of  $n < 1$ . Both Kissinger and Huang and co-workers calculated the reaction order using the same semi-empirical equation. Therefore, their calculated results are the same. In this calculation, the values of  $n$ ,  $E$ , and  $A$  of RDX are in fair agreement with the

Table 2  
Comparison of kinetic parameters obtained by various methods for  $n \neq 1$

	$\phi/(\text{°C min}^{-1})$	$n$	$E/(\text{kcal mol}^{-1})$	$A$
<b>Calcitic limestone</b>				
Isothermal TG [2]	0	0.55	44.0	$1.6 \times 10^6$
Yang and Steinberg [5]	6	0.55	44.0	$1.9 \times 10^6$
	10	0.57	43.0	$1.2 \times 10^6$
	15	0.56	44.0	$1.9 \times 10^6$
Liu et al. [6]		0.57		
Huang et al. [2]	6	0.56	45.0	$2.8 \times 10^6$
	10	0.58	44.4	$2.2 \times 10^6$
	15	0.59	43.6	$1.5 \times 10^6$
This work	6	0.58	35.3	$2.3 \times 10^4$
	10	0.51	27.4	$5.8 \times 10^2$
	15	0.60	33.7	$1.3 \times 10^4$
<b>RDX</b>				
Reich [9]	6	0.80	80.0	
Values in literature [3]	6	0.60	42.0	
	10	1.0	43.1–47.9	
	15		45.2	
			47.5	
		0	67.5	
Kissinger's method [1]			34.68	$8.3 \times 10^{12}$
Liu et al. [6]		0.6	32.5	$4.1 \times 10^{11}$
Huang and Wu [3]	6	0.85	44.9	$2.0 \times 10^{17}$
	10	0.93	44.8	$1.8 \times 10^{17}$
	15	0.96	46.8	$8.9 \times 10^{17}$
This work	6	0.896	48.7	$9.4 \times 10^{18}$
	10	0.890	33.2	$14. \times 10^{12}$
	15	0.993	61.7	$1.8 \times 10^{24}$
<b>HMX</b>				
Values in literature [3]	6	1.0	52.7	
	10	0.86	54.0	
	15		177.0	
			$228.0 \pm 24$	
		1.0	52.7 (liq.)	
		1.0	52.9 (vap.)	
Kissinger's method [1]			82.0	
Liu et al. [6]		0.86	54.0	$1.2 \times 10^{19}$
Huang and Wu [3]	6	0.67	51.7	$1.8 \times 10^{19}$
	10	0.82	50.0	$4.2 \times 10^{17}$
	15	0.95	57.8	$5.9 \times 10^{20}$
This work	6	0.880	98.12	$5.8 \times 10^{36}$
	10	0.968	98.23	$5.5 \times 10^{36}$
	15	0.998	111.16	$5.7 \times 10^{41}$
<b>Tetryl</b>				
Values in literature [3]	6	1.0	34.9	
	10	0.0	54.9	
	15	1.0	38.4	
Kissinger's method [1]			25.0	

Table 2 (continued)

	$\phi/(\text{°C min}^{-1})$	$n$	$E/(\text{kcal mol}^{-1})$	$A$
Liu et al. [6]		0.92	80.4	$2.5 \times 10^{34}$
Huang and Wu [3]	6	0.73	32.7	$7.9 \times 10^{12}$
	10	0.79	33.6	$1.7 \times 10^{13}$
	15	0.81	31.2	$1.2 \times 10^{12}$
This work	6	0.93	64.3	$5.1 \times 10^{27}$
	10	0.91	46.9	$2.3 \times 10^{19}$
	15	0.98	69.8	$3.9 \times 10^{29}$
PETN				
Values in literature [3]	6	1.0	33.0	
	10	1.0	47.0	
	15	1.0	47.0	
Reich [9]	6	$1.0 \pm 0.1$	$59.0 \pm 3$	$3.6 \times 10^{12}$
Kissinger's method [1]			33.0	$2.5 \times 10^{13}$
Liu et al. [6]		0.89	31.3	$1.8 \times 10^{12}$
Huang and Wu [3]	6	1.1	47.0	$7.0 \times 10^{19}$
	10	1.24	46.6	$3.1 \times 10^{19}$
	15	1.29	47.3	$4.5 \times 10^{19}$
Huang et al. [2]	6	0.95	38.3	$3.1 \times 10^6$
This work	6	0.95	36.4	$6.3 \times 10^{14}$
	10	0.97	35.1	$1.3 \times 10^{14}$
	15	0.96	37.7	$1.7 \times 10^{15}$
TNT				
Values in literature [3]	6	1.0	24.2	
	10		14.0	
	15	0	29.4	
Kissinger's method [1]			19.3	
Huang and Wu [3]	6	1.65	22.0	$7.1 \times 10^5$
	10	1.75	21.0	$2.9 \times 10^5$
	15	2.66		
This work	6	0.998	251.1	$4.1 \times 10^{93}$
	10	0.997	193.7	$1.8 \times 10^{70}$
	15	0.998	126.4	$3.7 \times 10^{44}$

literature data and calculations. These calculations of HMX give a better agreement of  $n$  to the experimental data than any other calculated results. However, the activation energies in these calculations are higher than previous data and the Huang method as the heating rates are 6 and  $10\text{°C min}^{-1}$ . When the heating is increased to  $15\text{°C min}^{-1}$  the calculated activation energy becomes lower than the experimental data but better than values from the Huang method. The values for  $n$  of Tetryl in the literature are unity for heating rates of 6 and  $15\text{°C min}^{-1}$  and zero for heating rates of  $10\text{°C min}^{-1}$ . The calculated results of  $n$  (0.88–0.98) are better than the Huang result of  $n$  from 0.73 to 0.81. The activation energy calculated from Huang et al.'s method is lower than the literature data, but the present calculation results are almost twice the reported values, except at a heating rate of  $10\text{°C min}^{-1}$ .

All of the  $n$  values of PETN shown in Refs. [3] and [9] are equal to unity. Huang used the modified Kissinger model to calculate the reaction order from their own DTA thermograms. All of their estimated  $n$  values are higher than unity. In our analysis, we found that the values of the characteristic temperatures are in the range of  $0.1 \leq (T_e - T_m)/(T_m - T_{i1}) \leq 11.96$ . Thus, from Eq. (17), the calculated values of  $n$  are less than unity. The activation of this calculation is  $36.4 \text{ kcal mol}^{-1}$  which is close to the literature value of  $33.0 \text{ kcal mol}^{-1}$  than obtained by the Kissinger or Huang methods at a heating rate of  $6^\circ\text{C min}^{-1}$ . However, a larger discrepancy with previously reported results at higher heating rates of 10 and  $15^\circ\text{C min}^{-1}$  was found. There are two reasons for these calculated results. One is the higher reaction order in previous predictions leading to the higher activation energy and pre-exponential factor evaluations. The other is that Eqs. (18) and (19) are functions of  $T_0$ ,  $T_m$ ,  $T_e$  and  $n$ . A slight change in  $T_0$  can produce a very large difference in the calculated results of  $E$  and  $A$ . In the Huang method, the characteristic temperatures  $T_m$ ,  $T_{i1}$ ,  $T_e$  and heating rate  $\phi$  are needed to evaluate their kinetic parameters. In the present calculation, we need one more variable, i.e.  $T_0$ , which is the intersection of the horizontal baseline and the DTA curve measured from the experimental DTA curves of Huang and Wu [3]. Unfortunately, a tiny observation error could cause a considerable calculated difference in  $E$  and  $A$  from Eqs. (19) and (20). The same results are also found for the TNT kinetic parameter calculations. The DTA curves shown in Huang et al. are too sharp to estimate the value of  $T_0$  very accurately. Therefore, the deviation of the calculated results from the reported data would be significant. Again, although Huang and Wu also obtained a reaction order of TNT greater than unity, we still use Eq. (17), i.e.  $n < 1$ , to evaluate the reaction order because the values of  $(T_e - T_m)/(T_m - T_{i1})$  are less than 11.96. All of the calculated  $n$  values are close to unity. Obviously, the Huang and Wu method cannot estimate the kinetic parameters of TNT for  $n$  higher than 2.

In the case of  $n > 1$ , general equations of Eqs. (21), (22), and (19) are used to evaluate the kinetic parameters,  $n$ ,  $E$ , and  $A$ , respectively. These equations can also be used in the category of  $n < 1$ . The valid conditions of calculation of these equations are  $0.58 \leq \Delta T_{i1}/\Delta T_m \leq 0.837$ . The calculated values of reaction order are  $0.1 \leq n \leq 10$ . So far, there is no relevant experimental data in the literature than can be used for the kinetic parameter calculations in this category. Even though Huang and Wu obtained values of reaction order greater than unity for PETN and TNT, the characteristic temperatures do not fall in the range  $0.58 \leq (\Delta T_{i1}/\Delta T_m) \leq 0.837$ . Thus we cannot calculate  $n$  and  $E$  using Eqs. (21) and (22). The calculated values of  $n$  for PETN and TNT in this work are less than unity.

#### 4. Conclusions

The characteristic temperature equations can be employed to evaluate the kinetic parameters,  $n$ ,  $E$ , and  $A$ , from a single DTA curve. For  $n < 1$ , Eqs. (17), (18), and (19) can be used to calculate  $n$ ,  $E$ , and  $A$ . For  $n = 1$ , Eqs. (32) and (25) can be used to calculate  $E$  and  $A$ . For  $n \neq 1$ , Eqs. (21), (22) and (19) are employed to calculate

$n$ ,  $E$ , and  $A$ . All of these equations are concise and can be used to calculate the kinetic parameters very quickly without any iteration. All of the kinetic parameters for decomposition reactions evaluated by the present method are in fair agreement with those in the literature, except for PETN and TNT.

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