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Ganguly method for the determination of kinetic parameters from differential thermal analysis curves

MAHUA KARMAKAR[1]*, Sk. AZHARUDDIN[2], SUPRIYA BARMAN[3], P.S. MAZUMDAR[1] and S. DORENDRAJIT SINGH[4]

[1]Department of Physics, Acharya Prafulla Chandra College, New Barrackpur, 24PGS (N), West Bengal - 700 131 (India).
[2]Raipur Shri Shri Ramkrishna Amrita Vidyalaya, Dakshin Raipur, Nodkhali, 24 PGS (S), West Bengal - 743 318 (India).
[3]Bhangar Balika Vidyalaya, Bhangar, 24PGS (S), West Bengal (India).
[4]Department of Physics, Manipur University, Canchipur, Imphal, Manipur - 795 003 (India).

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ABSTRACT

A method suggested by Ganguly is considered for the determination of kibnetic parameters of a differential thermal analysis (DTA) curve. The method is applied both to numerically computed and experimental DTA peaks and encouraging results have been obtained.

Key words: Differential thermal analysis, order of kinetics, pre-exponential factor, activation energy.

INTRODUCTION

The technique of differential thermal analysis (DTA) have been widely used as a tool to determine the kinetic parameters, namely the activation energy (E), pre-exponential factor (A) and the order of knetics (n). Moreover it is to be noted that DTA is an important technique for the study of complex solid state reactions and it has been also widely used in a number of areas such as the identification of different types of materials, the studies of the properties of thermal stability. For all these purpose an extensive knowledge of aforesaid kinetic parameters is essential. In this paper we critically analyse a method of extraction of kinetic parameters from DTA curve as suggested by Ganguly[1].

Theory

Following Luo[2] the kinetic equations for n-the order solid state reaction can be written as:

$$\frac{dx}{dt} = A(1-x)^n \exp\left(-\frac{E}{RT}\right) \quad ...(1)$$

Where x is the fraction of reaction completed in time *t*. In DTA, the temperature deviation T from the horizontal base line can be expressed by equation (1) as:

$$\Delta T = \beta A\left[1+(n-1)\frac{A}{\phi}\int_{T_o}^{T}\exp\left(-\frac{E}{RT}\right)dt\right]^{\frac{-n}{n-1}}\exp\left(-\frac{E}{RT}\right) \quad ...(2)$$

(n≠1)

and

$$\Delta T = \beta A\exp\left(-\frac{E}{RT}\right)\exp\left[-\frac{A}{\phi}\int_{T_o}^{T}\exp\left(-\frac{E}{RT}\right)dt\right] \quad ...(3)$$

(n = 1)

ϕ is the linear heating rat, T_0 is the initial temperature, T is the temperature at time /and β is

the proportionality constant. Now following Gartia et at[3] one can write

$$\int_{To}^{T} \exp\left(-\frac{E}{RT}\right) dt = \frac{E}{R}\left[\frac{E_2(u)}{u} - \frac{E_2(u_0)}{u_0}\right] \quad ...(4)$$

where

$$u = \frac{E}{RT}; u_0 = \frac{E}{RT_0}; E_2(u)$$

(μ) is the second exponential integral[4]. The peak temperature T_m of a DTA curve can be obtained from the equation

$$\left[\frac{d(\Delta T)}{dT}\right]_{T=Tm} = 0 \quad ..(5)$$

From equations (2), (3) and (5) the peak temperature T_m of a DTA curve can be obtained from the equation

$$\frac{E}{RT_m^2} - n\frac{A}{\phi}\exp\left(-\frac{E}{RT_m}\right)\left[1 + \frac{A(n-1)}{\phi}\int_{T_i}^{T}\exp\left(\frac{E}{RT'}\right)dT'\right] = 0 \quad ...(6)$$

From equations (1) – (6) it is possible to write

$$\frac{\Delta T}{(\Delta T)_m} = \exp[u_m - u + F(u, u_m)] \quad ...(7)$$

(n=1)

and

$$\frac{\Delta T}{(\Delta T)_m} = \exp(u_m - u)\left[1 - \frac{n-1}{n}F(u, u_m)\right]^{\frac{n}{n-1}} \quad ...(8)$$

(n≠1)

and

$(\Delta T)_m$ is the value of ΔT at peak temperature.

$$F(u, u_m) = u_m^2 \exp(u_m)\left[\frac{E_2(u_m)}{u_m} - \frac{E_2(u)}{u}\right] \quad ...(9)$$

Let T, be the temperature for which

Where $u_m = \frac{E}{RT_m}$ and $u = \frac{E}{RT}$

$$\frac{\Delta T}{(\Delta T)_m} = x$$

$T_x = T_x$ for $T_x < T_m$ ...(10)

$T_x = T_x$ for $T_x > T_m$ ....(11)

$$u_m^- = u_m - \ln x \frac{n}{n-1} ln\left[\left(1 - \frac{n-1}{n}\right)u_m^2 \exp(u_m)\left\{\frac{E_2(u_m)}{u_m} - \frac{E_2(u_x^-)}{u_x^-}\right\}\right] \quad ...(12)$$

$$u_x^+ = u_m - \ln\frac{R}{S} \quad ...(13)$$

With

$$R = Q - 1 + \left\{\frac{n-1}{n}\right\} u_m \exp(u_m) E_2(u_m) \quad ...(14)$$

$$S = \left(\frac{n-1}{n}\right) u_m^2 \exp(u_x^+)\frac{E_2(u_x^+)}{u_x^+} \quad ...(15)$$

and

$$Q = \left[\frac{1}{x}\exp(u_m - u_x^+)\right]^{\frac{n-1}{n}} \quad ...(16)$$

Again for n = 1 it follows that

$$u_x^- = \ln x + u_m + [1 + \exp(u_m) E_2(u_m)] - u_m^2 \frac{E_2(u_x^-)}{u_x^-} \quad ...(17)$$

and

$$u_z^- = u_m - \ln\left(\frac{-\ln x + u_m\{1+\exp(u_m)E_2(u_m)\} - u_z^+}{u_m^2 \exp(u_z^+) E_2(u_z^+)/u_z^+}\right) \quad ...(18)$$

Equations (12), (13), (17) and (18) have been solved by an iterative method. A plot of $\frac{u_x u_y}{u_m |u_y - u_x|}$ Against u_m was found to be linear, enabling us to write

$$E = \frac{CkT_m^2}{|T_x - T_y|} + DkT_m \quad ...(19)$$

Where $|T_x - T_y| = \tau$, δ or ω, τ is the half width of the rising side of the peak, δ is the half width in the falling side of the peak and $\omega = \tau + \delta$. All widths correspond to .

For a particular value of x, the co-efficients C, D on n. By using a method of least squares (Chakraborty[5]) each of the co-efficients C and D are expressed as a quadratic function of n so that

$\frac{\Delta T}{(\Delta T)_m} = x$

Where C_0, C_1, C_2, D_0, D_1 and D_2 are constants.

In order to determine order of kinetics, we define a shape index of a DTA peak as

$$S(x) = \frac{T_x^+ - T_m}{T_x^+ - T_x^-} \quad ...(21)$$

$$= \frac{u_x^-\left(u_m - u_x^+\right)}{u_x^- - u_x^+} \quad ...(22)$$

Using the technique of least squares5 S can be written as

$$S = a_0 n + a_1 n + a_2 n^2 \quad ...(23)$$

S can be directly evaluated from a DTA peak. Knowing S, n can be evaluated by eqn (23). Equation (23) being quadratic in n, gives two values of n. Out of the two values of n, one will be normally greater than 3 which is the maximum value of n and hence to be rejected. Knowing n, pre-exponential factor can be evaluated by using equation (6).

RESULT AND DISCUSSION

The value of C_i and D_i (I = 0-2) are presented in Table 1. In Table 2 we calculate the activation energies of some computer generated DTA peaks corresponding to the linear heating rate $\phi = 0.5^0$C sec $^{-1}$. It is evident from Table 2 there is close agreement with the input values of activation energies and activation energies as calculated by the present method for x = 1/2,2/3,4/5. Finally we apply the present method to calculate the other kinetic parameters namely order kinetics (n) and pre exponential factor (A) (Table 3). In this case also we have obtained a good agreement between the input and calculated values of the kinetic parameters.

Table 1: Co-efficient occurring in the expression for E (eqn. 20)

X	Relation	C_0	C_1	C_2	D_0	D_1	D_2
½	τ	1.019	0.504	-0.066	-1.059	-1.217	0.109
	δ	0.105	0.926	-0.048	0.154	-0.205	-0.128
	ω	1.124	1.427	-0.113	-0.902	-0.346	-0.061
2/3	τ	0.684	0.426	-0.055	-0.720	-1.21	0.098
	δ	0.146	0.683	-0.048	0.184	-0.432	-0.094
	ω	0.830	1.108	-0.103	-0.529	-0.607	-0.029
4/5	τ	0.449	0.342	-0.043	-0.480	-1.18	0.085
	δ	0.153	0.487	-0.041	0.180	-0.606	-0.062
	ω	0.602	0.829	-0.084	-0.293	-0.777	-0.006

Encouraged by out findings in the case of computer generated DTA peaks we apply the present method to experimental DTA peaks of different systems namely Georgia Kaolinite[6], Eureka halloysite[6], Cyclo tri methylene trinitrane (RDX)[7], trinitron toluene (TNT)[7], Ni $[(mpipz)_2 (NCS)_2]$8 (mpipz stands for N-methylipiprazine). The results are presented in Table 4. The activation energies as reported in Table 3 is average of the values of E_τ E_δ and E_ω calculated respectively for x =n 1/, 2/3, 4/

Table 2: Activation energies of some computer generated DTA peaks

Input values of						
E (KJ)	**N (Sec^{-1})**	**A**	**X**	**E_τ**	**E_δ**	**E_ω**
			1/2	153.72	154.20	154.11
153.012	0.7	10^{13}	2/3	154.18	153.95	154.25
			4/5	153.86	154.14	153.91
			1/2	153.82	154.54	153.96
153.012	1.0	10^{13}	2/3	154.12	153.93	154.38
			4/5	154.29	154.14	153.76
			1/2	154.69	154.78	154.69
153.012	1.5	10^{13}	2/3	153.59	154.63	153.97
			4/5	153.69	153.82	154.95
			1/2	154.39	153.91	154.22
153.012	2.0	10^{13}	2/3	154.68	154.49	153.97
			4/5	153.91	154.17	154.88

Table 3: Order of kinetics (n) and pre exponential factor (A) of some computer generated DTA peaks

Input Values of			Calculated Values of		
E (KJ)	**n**	**A (Sec^{-1})**	**S**	**n**	**A (Sec^{-1})**
153.012	0.7	10^{13}	0.362	0.71	1.07×10^{13}
153.012	1.0	10^{13}	0.421	1.06	2.37×10^{13}
153.012	1.5	10^{13}	0.481	1.53	1.54×10^{13}
153.012	2.0	10^{13}	0.524	1.98	7.42×10^{13}

Table 4: Kinetic parameters of some experimental DTA peaks

Compound	Heating rate	E (ϕ)	n (KJ)	A (sec^{-1})
Georgia Kaolinite[6]	6	153.01	0.98	1.75×10^{12}
Eureka Halloysite[6]	6	158.21	1.02	2.52×10^{9}
RDX[7]	15	195.26	0.97	1.43×10^{12}
TNT[7]	10	88.284	1.67	1.82×10^{8}
Ni $[(mpipz)_2(NCS)_2]$[8]	10	143.94	1.45	7.83×10^{6}

5. The values of the kinetic parameters presented in Table 4 are in fair agreement with those reported in the literature.

CONCLUSION

In the present paper as suggested by Ganguly we have analyzed a method of determination of kinetic parameters associated with a DTA curve. The suitability of the present method is judged by applying it to extract the kinetic parameters of computer simulated and experimental DTA curves. In the present paper we have also presented expressions involving temperatures at 2/3 and 4/5 along with those at ½ considering the fact that the upper half of a DTA peak is expected to be free from interference of satellite peaks. So it is possible to use Ganguly method even if the DTA peak is not well isolated.

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