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The importance of the inflection point in nonisothermal analysis: New derivative methods

S.G. Viswanath[a,*], M.C. Gupta[b]

[a] *Laxminarayan Institute of Technology, Nagpur University, Nagpur 440010, India*
[b] *Department of chemistry, Nagpur University, Nagpur, India*

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Abstract

New derivative methods have been developed using inflection points. More accurate nonisothermal kinetic parameters can be obtained by using these methods. One of the methods provides a more accurate order of reaction than the Freeman–Carroll method. The application of these methods to polymer decomposition is also presented. © 1997 Elsevier Science B.V.

1. Introduction

Isothermal procedures for determining the kinetic parameters of simple reactions are relatively simple, but a single nonisothermal procedure may replace many isothermal experiments. A wide variety of methods have been reported for the analysis of TGA curves, each method claiming special advantages. These may be classified as derivative and integral methods. Among the derivative methods, the Freeman–Carroll [1] method is widely used despite its limited precision [2] because it is the only method available for estimation of the order of reaction. This method also allows the estimation of activation energy, but suffers from disadvantages [2–4]. In the method of multiple heating rates [5,6], the analytical form $f(\alpha)$, where α is the fraction decomposed, is to be assumed in order to obtain nonisothermal kinetic parameters. In the Sharp–Wentworth [2] method, if a correct order is assumed and substituted in the Arrhenius temperature dependence equation, the logarithmic plot is linear. Nonisothermal kinetic parameters can be determined from such a plot.

Doyle [7] proposed a curve fitting method for single thermogram by assuming an approximation which reduces the speculative nature of the method for estimating nonisothermal kinetic parameters. In all integral methods, a correct assumption of the order of reaction, depending on the equation used, gives linear plots from which the nonisothermal kinetic parameters are estimated. Coats and Redfern [3] used an asymptotic approximation for the evaluation of exponential integral of the Arrhenius equation. Several methods of varied heating rates for the estimation of activation energy have been described [8–11]; however, all available methods almost always involve the assumption that reaction follows a simple reaction order.

In this communication an attempt is made to develop a new differential method to estimate the order of reaction, nonisothermal kinetic parameters, and to modify the Freeman–Carroll as well as Sharp–

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*Corresponding author.

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Wentworth methods. In a TG curve at the inflection point, the value of (dα/dT) is maximum and related to the order and activation energy of the reaction. Hence, the possibility of using this as a reference point to develop new equations has been explored.

TG data of calcium oxalate, copper sulfate, high-impact polystyrene (HIPS), polycarbonate bisphenol A (PB) and vanadium pentoxide coated with HIPS and PB separately, as described by Jais and Gupta [12], are used in this present study.

2. Method of obtaining derivatives

Let α be the fraction decomposed at temperature, T, then α may be expressed as a polynomial in T as,

$$\alpha^m = X_1 + X_2 + X_2T + X_3T^2 + \cdots + X_pT^{p-1} \tag{1}$$

where p is the total number of data points, X_1, $X_2, ..., X_p$ are the coefficients of the polynomial and m is a real number which can be varied till the criteria mentioned by Viswanath et al. [4] are satisfied. Generally, m is varies between 1.00 to −1.00, but cannot be zero. In other words, the degree of the polynomial is equal to one less than the total number of data points. The coefficients of the polynomial are obtained by nonlinear regression method (least squares method) as,

$$\sum_{i=0}^{p-1} T^i\alpha^m = X_1\sum_{i=0}^{p-1} T^{i+1} + X_2\sum_{i=0}^{p-1} T^{i+2} + \cdots + X_p\sum_{i=0}^{p-1} T^{p+i-1} \tag{2}$$

Eq. (2) generates p equations for different values of i. Each term in each equation and α are considered as the elements of $p\times(p+1)$ matrix. The coefficients of the polynomial are obtained by solving the matrix as described earlier [4].

Fitting a collocation (interpolating) polynomial to irregular data leads to very poor estimates of derivatives. Even a slight error in the data is magnified [13]. This regression polynomial does not collocate, but passes between the data points and provides smoothing. This smoother function gives better estimates of derivatives [13]. The higher the degree of the polynomial the lower the error in the determination of derivatives. Hence, the (p−1)th degree polynomial is considered here. Taking the dependent variable, in which m is varied till minimum average percent deviation (A.D) and maximum correlation coefficient (C.C) is obtained, further reduces the error in these estimates. The statistical definition for the terms C.C and A.D are given in Appendix A This polynomial is differentiated and the T values substituted to obtain the derivatives. Since this polynomial represents the data in all respects, and the derivatives can also be obtained, it is possible to estimate $(1-\alpha)$ and fractional.

3. Derivative methods

The fraction decomposed, α is defined as,

$$\alpha = \frac{(W_0 - W_T)}{(W_0 - W_f)} \tag{3}$$

where W_0, W_f, W_T are the initial mass, final mass and mass of the substance at temperature T, respectively, and the Arrhenius equation is written as

$$\mathrm{d}\alpha/\mathrm{d}T = (1-\alpha)^n(A/\beta)\mathrm{e}^{-E_\alpha/RT} \tag{4}$$

where n, A, β, and E_α are the order, pre-exponential factor, rate of heating and activation energy of a reaction, respectively. The second derivative of Eq. (4) will be,

$$\mathrm{d}^2\alpha/\mathrm{d}T^2 = -n(1-\alpha)^{n-1}(A/\beta)\mathrm{e}^{E_\alpha/RT}(\mathrm{d}\alpha\mathrm{d}T) + (1-\alpha)^n(A/\beta)(E_\alpha/RT^2)\mathrm{e}^{-E_\alpha/RT} \tag{5}$$

At the inflection point the second derivative, $(\mathrm{d}^2\alpha/\mathrm{d}T^2) = 0$ and (dα/dT) is maximum. Hence Eq. (5) can be written as

$$(\mathrm{d}\alpha/\mathrm{d}T)_s = \{(1-\alpha_s)/n\}(E_\alpha/RT_s^2) \tag{6}$$

The subscript, s defines the quantities at inflection point and Eq. (6) is rearranged as,

$$(E_\alpha/R) = \{nT_s^2/(1-\alpha_s)\}(\mathrm{d}\alpha/\mathrm{d}T)_s \tag{7}$$

Eq. (4) at inflection point can be written as

$$(\mathrm{d}\alpha/\mathrm{d}T)_s = (1-\alpha_s)^n(A/\beta)\mathrm{e}^{-E_\alpha/RT_s} \tag{8}$$

Using (Eqs. (6)–(8)), we may develop three different methods which will be referred as (1) – the reference, (2) – the absolute, and (3) – the standard methods.

The inflection point is very sensitive to temperature. Hence, search for the maximum derivative is carried with 0.01 K temperature difference. Such search for a maximum derivative manually from a TG curve is a tedious process. Therefore, a computer program written in Turbo Pascal language is used to determine the maximum derivative and the corresponding temperature as well as fractional residue, $(1-\alpha)$.

3.1. *The reference method*

In this method, differences are obtained by subtracting the logarithmic form of Eq. (8) from the logarithmic form of Eq. (4). Since Eq. (8) is taken relative to Eq. (4) at the inflection point, we may also call this method as the relative method. The general equation of this method is written as

$$\ln\{(\mathrm{d}\alpha/\mathrm{d}T)_s/(\mathrm{d}\alpha/\mathrm{d}T)\} = n\ln\{(1-\alpha_s)/(1-\alpha)-(E_\alpha/R)\{1/T_s-1/T\} \tag{9}$$

Eq. (9) may be written as

$$\frac{\Delta\ln\{(\mathrm{d}\alpha/\mathrm{d}T)\}}{\Delta\ln(1-\alpha)} = \frac{(E_\alpha/R)\Delta(1/T)}{\Delta\ln(1-\alpha)} + n \tag{10}$$

The plot of $\{\Delta\ln(\mathrm{d}\alpha/\mathrm{d}T)/\Delta\ln(1-\alpha)\}$ vs. $\{\Delta(1/T)/\Delta\ln(1-\alpha)\}$ results in a straight line from which the activation energy, E_α, and the order of reaction, n, can be obtained. These values along with the rate of heating, β, are substituted in Eq. (8) to obtain the pre-exponential factor. When n is substituted in Eq. (7), we get the expected activation energy for the reaction. If the activation energy from the slope and the expected activation energy are same, or nearly the same within experimental error, one can take this as the correct order of reaction. Thus, this method provides a good verification for the estimates of nonisothermal kinetic parameters. Further, the accuracy can be cross-checked by finding C.C. and A.D. This method avoids ambiguity of selecting a data point to find differences. Table 1 gives results of nonisothermal parameters of some compounds and Fig. 1 gives plots for these compounds. The activation energy, E_α, is expressed in kJ mol^{-1} and the pre-exponential factor, A, in s^{-1}.

3.2. *The absolute method*

In this method, the (E_α/R) value from Eq. (7) is substituted in Eq. (4), and then the logarithmic form of the equation can be written as

$$\ln(\mathrm{d}\alpha/\mathrm{d}T) = n\{\ln(1-\alpha)-\phi/T\} + \ln(A/\beta) \tag{11}$$

where $\phi = \{T^2/(1-\alpha_s)\}(\mathrm{d}\alpha/\mathrm{d}T)_s$. The plot of $\ln(\mathrm{d}\alpha/\mathrm{d}T)$ vs. $\{\ln(1-\alpha)-\phi/T\}$ gives a linear plot with a slope n, the order of reaction and intercept (A/β). By substituting the value of n in Eq. (7), E_α is obtained. Nonisothermal kinetic parameters estimated by this method for some compounds are presented in Table 2 and plots are shown in Fig. 2. For the accuracy of this method, one has to rely on C.C. and A.D.

3.3. *The standard method*

The order of reaction, n, obtained from the first and second methods is substituted in the logarithmic form of Eq. (4) and the general equation is written as

$$\ln(k) = (E_\alpha/R)(1/T) + \ln(A/\beta) \tag{12}$$

where $k = (\mathrm{d}\alpha/\mathrm{d}T)/(1-\alpha)^n$. The plot of $\ln(k)$ vs. $(1/T)$ results in a straight line, from which E_α and A can be determined. This method avoids searching for

Table 1
Nonisothermal kinetic parameters by the reference method

S. No.	Name of compound	Order of reaction	E_α from slope	E_α from Eq. (7)	A	A.D	C.C.
1	CaC_2O_4	1.1	315.7	315.8	1.0×10^{20}	8.77	0.9999
2	$CuSO_4$	1.9	300.8	265.8	1.1×10^{14}	1.96	0.9993
3	HIPS	1.1	118.8	119.3	5.0×10^{7}	5.48	0.9996
4	PB	2.1	363.3	363.7	2.4×10^{23}	2.68	0.9992
5	PB V_2O_5	1.2	178.7	178.1	1.0×10^{11}	4.53	0.9988
6	HIPS V_2O_5	0.6	158.1	158.6	1.0×10^{11}	2.87	0.9999

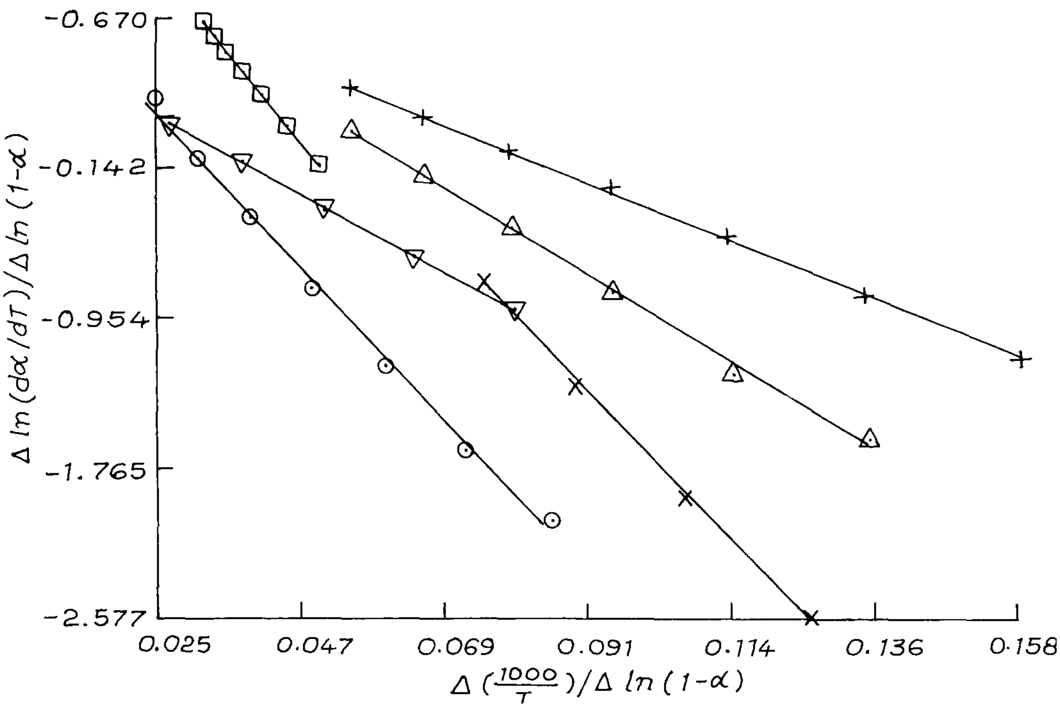

Fig. 1. Plots from the reference method: 1) ⊙ CaC_2O_4; 2) × $CuSO_4$; 3) + HIPS; 4) □ PB; 5) △ PB V_2O_5; and 6) ▽ HIPS V_2O_5.

Table 2
Nonisothermal kinetic parameters by the absolute method

S. No.	Name of compound	Order of reaction	E_α from Eq. (7)	A	A.D	C.C
1	CaC_2O_4	1.1	306.8	2.2×10^{19}	0.52	0.9990
2	$CuSO_4$	2.3	315.9	8.5×10^{14}	0.31	0.9991
3	HIPS	1.1	120.1	6.6×10^{7}	0.08	0.9999
4	PB	2.1	365.0	3.2×10^{23}	0.19	0.9996
5	PB V_2O_5	1.2	177.5	8.1×10^{10}	0.23	0.9996
6	HIPS V_2O_5	0.6	158.1	1.0×10^{10}	0.05	1.0000

correct order of reaction by the trial and error method. Table 3 lists the results obtained by using n values from the first and second methods in case of non-isothermal kinetic parameters for some compounds. But Fig. 3 shows plots drawn with n values obtained the from absolute method.

For zero order reactions, the logarithmic form of Eq. (4) is written as,

$$\ln(\mathrm{d}\alpha/\mathrm{d}T) = -(E_\alpha/R)(1/T) + \ln(A/\beta) \quad (13)$$

The plot of $\ln(\mathrm{d}\alpha/\mathrm{d}T)$ vs. $(1/T)$ results in a straight line from which both E_α and A can be determined.

4. Results and discussion

If the data of Tables 1 and 2 are compared, the A.Ds are very high for the reference method than for the absolute method; moreover, correlations are better for the absolute method than for the reference method. If the results of Tables 1 and 3, which contain results obtained by substituting the order of reaction from the reference method, are compared, the deviations go down to a minimum in the standard method and correlation coefficients are almost one. Similarly, if the data of Tables 1 and 3, that contain results

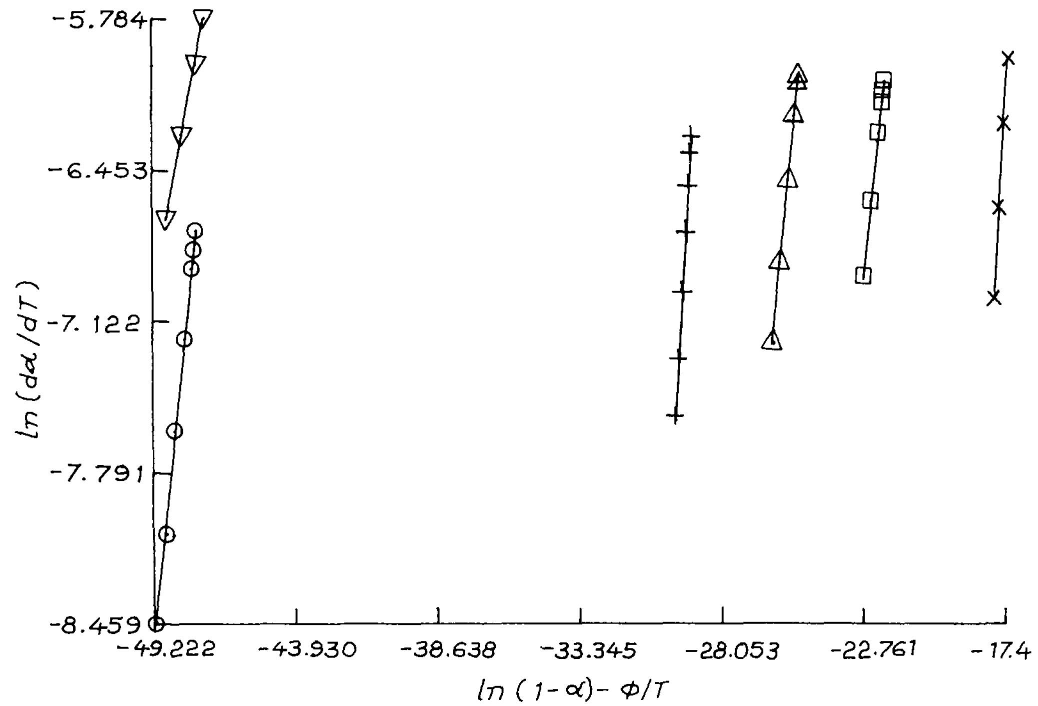

Fig. 2. Plots from the absolute method: 1) ○ CaC_2O_4; 2) × $CuSO_4$; 3) + PB; 4) □ HIPS; 5) △ PB V_2O_5; and 6) ▽ HIPS V_2O_5.

Table 3
Nonisothermal kinetic parameters by the standard method

S. No.	Name of compound	n used from first method				n used from second method			
		E_α	A	A.D	C.C	E_α	A	A.D	C.C
1	CaC_2O_4	307.2	2.4×10^{19}	0.58	0.9996	315.8	4.6×10^{19}	0.33	0.9996
2	$CuSO_4$	316.8	9.6×10^{14}	0.34	0.9996	306.3	2.3×10^{14}	0.11	0.9999
3	HIPS	120.0	6.4×10^{7}	0.10	1.0000	119.4	5.8×10^{7}	0.07	1.0000
4	PB	365.2	2.3×10^{23}	0.24	0.9999	361.3	1.7×10^{23}	0.22	0.9999
5	PB V_2O_5	177.9	8.7×10^{10}	0.23	0.9997	178.2	9.2×10^{10}	0.23	0.9997
6	HIPS V_2O_5	158.1	1.0×10^{10}	0.06	1.0000	158.4	1.1×10^{10}	0.04	1.000

obtained by substituting order of reaction from the absolute method, are compared, there is not much change in deviation values as well as in the correlation coefficients. Hence, it is better to obtain the order of reaction from the absolute method and use it in the standard method to get more accurate nonisothermal kinetic parameters.

In Table 4, the order of reaction and activation energy obtained with respect to different data points are presented for calcium oxalate and HIPS as used in the Freeman–Carroll method.

If this table is examined carefully, the activation energy reaches a minimum, and thereafter rises. It is thus proposed to determine Δ values with respect to the inflection point in the reference method. The reference method not only allows the estimation of the activation energy and order of reaction but also the pre-exponential factor.

Horowitz and Metzer [14] proposed an integral method for the determination of nonisothermal kinetic parameters using an inflection point. They derived the following relationship between the order of reaction

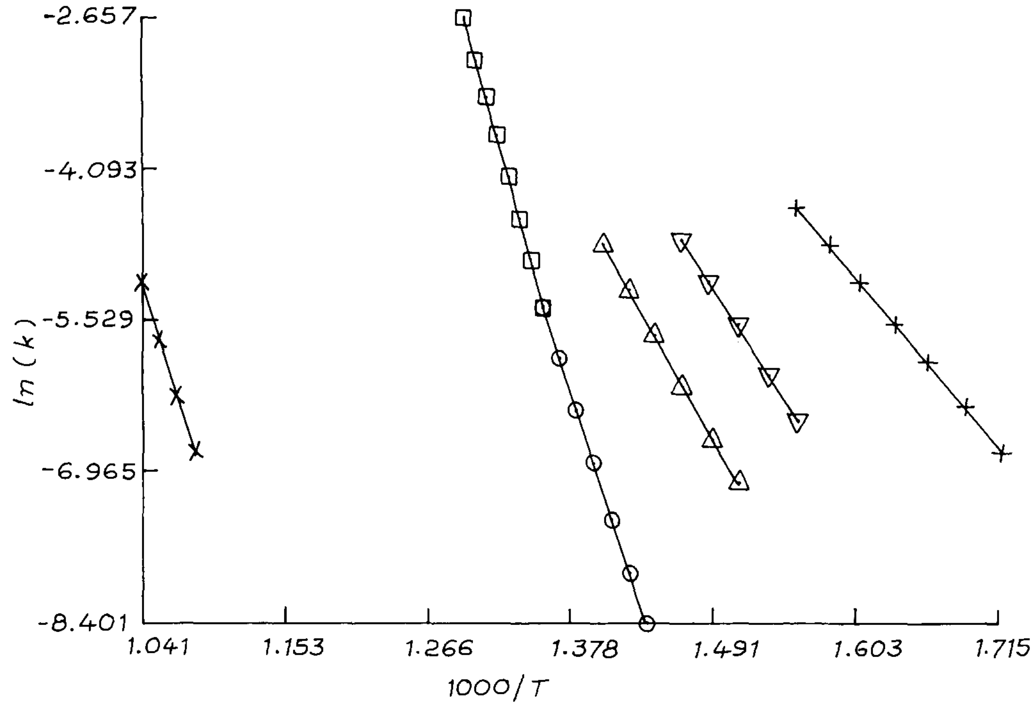

Fig. 3. Plots from the standard method: 1) ○ CaC_2O_4; 2) × CuS_O; 3) + HIPS; 4) □ PB; 5) △ PB V_2O_5; and 6) ▽ HIPS V_2O_5.

Table 4
Activation energy and order of reaction obtained with respect to different data points

Points selected to find difference (Δ's)	Calcium oxalate		HIPS	
	Activation energy	Order of reaction	Activation energy	Order of reaction
2	333	1.3	122	1.1
3	408	1.8	122	1.1
4	409	1.8	127	1.2
5	381	1.6	116	1.1
6	369	1.5	119	1.1
7	343	1.3	122	1.1
8	342	1.3	123	1.1
9	359	1.5	—	—
Inflection point	316	1.1	119	1.1

and fraction decomposed at the inflection point.

$$(1-\alpha_s) = n^{1/(1-n)} \qquad (14)$$

The order of reaction calculated from Eq. (14) is higher than that obtained by the other methods. Dharwadkar and Karkhanavala [15] opined that large variations are due to the inherent limitations in the method.

MacCallum and Tanner [16] claimed that the kinetic parameters obtained by nonisothermal methods are in poor agreement with the values obtained by isothermal methods for thermal decomposition of polymers, at least in some cases. They also believed that the basic equation in the dynamic method might be inaccurate. The poor agreement between the results of these methods may be due to other reactions, such as side reactions or parallel consecutive reactions, etc. taking place due to a constant change of temperature. It is apparent from Eq. (6), which is independent of the heating rate, that the nonisothermal kinetic parameters depend on the inflection point, and not on the heating rate.

Appendix A

If a_i and Y_i are the experimental value and the value obtained from a regression line or curve, respectively, for p data points, the correlation coefficient (C.C) is then defined as

$$\mathrm{C.C} = r_1/(r_2.r_3)^{1/2}$$

where r_1, r_2 and r_3 defined as

$$r_1 = \Sigma\alpha_i \cdot Y_i/p - \Sigma Y_i \Sigma\alpha_i/p^2;$$

$$r_2 = \Sigma Y_i^2/p - (\Sigma Y_i/p)^2 \text{ and}$$

$$r_3 = \Sigma\alpha_i/p - (\Sigma\alpha_i/p)^2.$$

The average percent deviation (A.D) is defined as

$$\mathrm{A.D} = [\Sigma_{\mathrm{abs}}\{(\alpha_i - Y_i)/\alpha_i\} \times 100]/p$$

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