

## EVALUATION OF KINETIC PARAMETERS FROM THERMOGRAVIMETRIC CURVES. PART III. MODIFICATIONS OF THE DIFFERENTIAL CORRECTION METHOD \*

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### ABSTRACT

Two new differential correction methods for evaluating kinetic parameters from thermogravimetric data, based on the minimization of the sum of squares difference between the observed and calculated temperatures, and between the observed and calculated  $d\alpha/dT$  in differential form, respectively, are proposed. The new methods were tested by the experimental data of acid-catalyzed iodination of acetone with satisfactory results.

### INTRODUCTION

The mechanisms of solid-phase reactions are very complicated. According to Šesták and Berggren [1] five types of mechanism have been identified. A general formula is given

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p \quad (1)$$

where  $\alpha$  represents degree of conversion at time  $t$ ,  $k$  is the rate constant which is a function of absolute temperature  $T$ . The five known types of mechanism are  $m$ ,  $n$ ,  $p$ ,  $mn$  and  $np$ . Many methods and modifications have been proposed to evaluate the kinetic parameters of solid-phase reactions from thermogravimetric (TG) traces [2–23]. Chen and Fong have proposed a combined numerical method [22] in which the secondary  $d\alpha/dT$  values are first treated by the linear least-squares method [24] to determine the correct type of reaction mechanism and the approximate values of its kinetic

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parameters. The resultant parameters are subsequently improved by the differential correction (DC) method using the more exact experimental data of  $\alpha$  and  $T$ . The method has been applied successfully to analyze a set of synthetic data and thermal dehydration data of gypsum by Šesták and Berggren [1] and also the TG data for the thermal dehydroxylation of  $\text{Mg}(\text{OH})_2$  [23]. However, the method is not always successful, divergence may occur in some cases especially when it is applied to analyze solution data [21]. This paper reports two modifications to improve the combined numerical method.

## RESULTS AND DISCUSSION

The basic equation for a dynamic kinetic method is

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{C} \int_0^T e^{-E/RT} dT \quad (2)$$

where  $A$  is the pre-exponential factor for the Arrhenius equation,  $C$  is the heating rate and  $E$  the activation energy. The left-hand side of the above equation may be symbolized by  $F$  and the right-hand side by  $G$ , i.e.

$$F(\alpha_i, m, n, p) = G(T_i, A, E) \quad (3)$$

where  $m, n, p$  have been defined by eqn. (1). In the original DC method [22] the principle is to find a set of kinetic parameters  $m, n, p, A$  and  $E$  such that the sum of the square difference

$$S = \sum [F(\alpha_i, m, n, p) - G(T_i, A, E)]^2 \quad (4)$$

is minimum.

The reason for divergence encountered in this method may be explained as follows. Suppose a set of parameters  $m, n$  and  $p$  gives a value of  $F$  smaller than the desired accuracy, then any set of  $A$  and  $E$  which gives a  $G$  value smaller than, but not necessarily close to  $F$ , would yield  $S$  and satisfy the condition mathematically, but might not give rational parameters. This would cause overflow or underflow in the analysis computation.

### *Modification I. Minimization with respect to temperature*

Now let us consider the problem in a slightly different way. For a certain set of parameters, a graph of  $\alpha$  vs.  $T$  may be calculated from eqn. (2). An  $\alpha$  vs.  $T$  curve may also be constructed from the thermal analysis data. For a given value of  $\alpha_i$ , there are two values of  $T$ ;  $T_c^i$  read from the experimental curve and  $T_c^i$  from the calculated curve. The best set of parameters must be those which would make the following sum of least-squares difference

$$S_T = \sum [T_c^i - T_c(\alpha_i, m, n, P, A, E)]^2 \quad (5)$$

a minimum. In this treatment  $T_e^i$  are experimental values which are definite and real. Therefore, there could only be one set of kinetic parameters that would give  $S_T$  a minimum value, and no divergence is expected to occur. The kinetic parameters obtained by minimizing  $S_T$  are believed to be more accurate than those obtained by minimizing  $S$  in eqn. (4). Since it has been reported that kinetic parameters evaluated by minimizing  $S$  give differences of  $(T_e - T_c)$  larger at lower values of  $\alpha$  than at higher values [23], minimization of  $S_T$  should be a better criterion than the other.

The necessary conditions for minimizing eqn. (5) are

$$\frac{\partial S_T}{\partial m} = 0; \frac{\partial S_T}{\partial n} = 0; \frac{\partial S_T}{\partial p} = 0; \frac{\partial S_T}{\partial A} = 0 \text{ and } \frac{\partial S_T}{\partial E} = 0$$

Let  $m^0, n^0, p^0, A^0$  and  $E^0$  be the approximate values of the corresponding parameters derived from the linear least-squares method as described in a previous paper [22], and  $\Delta m, \Delta n, \Delta p, \Delta A$  and  $\Delta E$  be the differential corrections that must be added to the corresponding approximate parameters in order to achieve the condition of "best fit", namely

$$m = m^0 + \Delta m \quad (6)$$

$$n = n^0 + \Delta n \quad (7)$$

$$p = p^0 + \Delta p \quad (8)$$

$$A = A^0 + \Delta A \quad (9)$$

$$E = E^0 + \Delta E \quad (10)$$

substitute these equations into eqn. (5), apply Taylor's expansion and neglect the terms which have higher powers in  $\Delta m, \Delta n, \Delta p, \Delta A$  and  $\Delta E$ , we have

$$S_T = \sum \left[ T_e^i - \left( T(\alpha_i, m^0, n^0, p^0, A^0, E^0) + \left( \frac{\partial T}{\partial m} \right)_i \Delta m + \left( \frac{\partial T}{\partial n} \right)_i \Delta n + \left( \frac{\partial T}{\partial p} \right)_i \Delta p + \left( \frac{\partial T}{\partial A} \right)_i \Delta A + \left( \frac{\partial T}{\partial E} \right)_i \Delta E \right)^2 \right] \quad (11)$$

In eqn. (11) we write  $T$  instead of  $T_c$  for the sake of simplicity.

The necessary conditions to make  $S_T$  a minimum are

$$\frac{\partial S_T}{\partial (\Delta m)} = \sum \left[ T_e^i - \left( T^0 + \left( \frac{\partial T}{\partial m} \right)_i \Delta m + \left( \frac{\partial T}{\partial n} \right)_i \Delta n + \left( \frac{\partial T}{\partial p} \right)_i \Delta p + \left( \frac{\partial T}{\partial A} \right)_i \Delta A + \left( \frac{\partial T}{\partial E} \right)_i \Delta E \right) \right] \left( \frac{\partial T}{\partial m} \right)_i = 0 \quad (12)$$

$$\frac{\partial S_T}{\partial (\Delta n)} = 2 \sum \left[ T_e^i - \left( T^0 + \left( \frac{\partial T}{\partial m} \right)_i \Delta m + \left( \frac{\partial T}{\partial n} \right)_i \Delta n + \left( \frac{\partial T}{\partial p} \right)_i \Delta p + \left( \frac{\partial T}{\partial A} \right)_i \Delta A + \left( \frac{\partial T}{\partial E} \right)_i \Delta E \right) \right] \left( \frac{\partial T}{\partial n} \right)_i = 0 \quad (13)$$

$$\frac{\partial S_T}{\partial(\Delta p)} = 2 \sum \left[ T_e^i - \left( T^0 + \left( \frac{\partial T}{\partial m} \right)_i \Delta m + \left( \frac{\partial T}{\partial n} \right)_i \Delta n + \left( \frac{\partial T}{\partial p} \right)_i \Delta p + \left( \frac{\partial T}{\partial A} \right)_i \Delta A + \left( \frac{\partial T}{\partial E} \right)_i \Delta E \right] \left( \frac{\partial T}{\partial p} \right)_i = 0 \quad (14)$$

$$\frac{\partial S_T}{\partial(\Delta A)} = 2 \sum \left[ T_e^i - \left( T^0 + \left( \frac{\partial T}{\partial m} \right)_i \Delta m + \left( \frac{\partial T}{\partial n} \right)_i \Delta n + \left( \frac{\partial T}{\partial p} \right)_i \Delta p + \left( \frac{\partial T}{\partial A} \right)_i \Delta A + \left( \frac{\partial T}{\partial E} \right)_i \Delta E \right] \left( \frac{\partial T}{\partial A} \right)_i = 0 \quad (15)$$

$$\frac{\partial S_T}{\partial(\Delta E)} = 2 \sum \left[ T_e^i - \left( T^0 + \left( \frac{\partial T}{\partial m} \right)_i \Delta m + \left( \frac{\partial T}{\partial n} \right)_i \Delta n + \left( \frac{\partial T}{\partial p} \right)_i \Delta p + \left( \frac{\partial T}{\partial A} \right)_i \Delta A + \left( \frac{\partial T}{\partial E} \right)_i \Delta E \right] \left( \frac{\partial T}{\partial E} \right)_i = 0 \quad (16)$$

where  $T^0$  denotes  $T(\alpha_i, m^0, n^0, p^0, A^0, E^0)$ . Equations (12)–(16) lead to five simultaneous equations which are linear to the differential corrections. These five equations can be expressed in the following form

$$[\mathbf{U}][\Delta] = [\mathbf{W}] \quad (17)$$

where  $[\mathbf{U}]$ ,  $[\Delta]$  and  $[\mathbf{W}]$  are matrices which are defined as follows:

$$[\mathbf{U}] = \begin{bmatrix} \sum \left( \frac{\partial T}{\partial m} \right)_i^2 & \sum \left( \frac{\partial T}{\partial n} \right)_i \left( \frac{\partial T}{\partial m} \right)_i & \sum \left( \frac{\partial T}{\partial p} \right)_i \left( \frac{\partial T}{\partial m} \right)_i & \sum \left( \frac{\partial T}{\partial A} \right)_i \left( \frac{\partial T}{\partial m} \right)_i & \sum \left( \frac{\partial T}{\partial E} \right)_i \left( \frac{\partial T}{\partial m} \right)_i \\ \sum \left( \frac{\partial T}{\partial n} \right)_i \left( \frac{\partial T}{\partial m} \right)_i & \sum \left( \frac{\partial T}{\partial n} \right)_i^2 & \sum \left( \frac{\partial T}{\partial p} \right)_i \left( \frac{\partial T}{\partial n} \right)_i & \sum \left( \frac{\partial T}{\partial A} \right)_i \left( \frac{\partial T}{\partial n} \right)_i & \sum \left( \frac{\partial T}{\partial E} \right)_i \left( \frac{\partial T}{\partial n} \right)_i \\ \sum \left( \frac{\partial T}{\partial p} \right)_i \left( \frac{\partial T}{\partial m} \right)_i & \sum \left( \frac{\partial T}{\partial p} \right)_i \left( \frac{\partial T}{\partial n} \right)_i & \sum \left( \frac{\partial T}{\partial p} \right)_i^2 & \sum \left( \frac{\partial T}{\partial A} \right)_i \left( \frac{\partial T}{\partial p} \right)_i & \sum \left( \frac{\partial T}{\partial E} \right)_i \left( \frac{\partial T}{\partial p} \right)_i \\ \sum \left( \frac{\partial T}{\partial A} \right)_i \left( \frac{\partial T}{\partial m} \right)_i & \sum \left( \frac{\partial T}{\partial A} \right)_i \left( \frac{\partial T}{\partial n} \right)_i & \sum \left( \frac{\partial T}{\partial A} \right)_i \left( \frac{\partial T}{\partial p} \right)_i & \sum \left( \frac{\partial T}{\partial A} \right)_i^2 & \sum \left( \frac{\partial T}{\partial E} \right)_i \left( \frac{\partial T}{\partial A} \right)_i \\ \sum \left( \frac{\partial T}{\partial E} \right)_i \left( \frac{\partial T}{\partial m} \right)_i & \sum \left( \frac{\partial T}{\partial E} \right)_i \left( \frac{\partial T}{\partial n} \right)_i & \sum \left( \frac{\partial T}{\partial E} \right)_i \left( \frac{\partial T}{\partial p} \right)_i & \sum \left( \frac{\partial T}{\partial E} \right)_i \left( \frac{\partial T}{\partial A} \right)_i & \sum \left( \frac{\partial T}{\partial E} \right)_i^2 \end{bmatrix} \quad (18)$$

$$[\Delta] = \begin{bmatrix} \Delta m \\ \Delta n \\ \Delta p \\ \Delta A \\ \Delta E \end{bmatrix} \quad (19)$$

$$[\mathbf{W}] = \begin{bmatrix} \sum (T_e^i - T^0) \left( \frac{\partial T}{\partial m} \right)_i \\ \sum (T_e^i - T^0) \left( \frac{\partial T}{\partial n} \right)_i \\ \sum (T_e^i - T^0) \left( \frac{\partial T}{\partial p} \right)_i \\ \sum (T_e^i - T^0) \left( \frac{\partial T}{\partial A} \right)_i \\ \sum (T_e^i - T^0) \left( \frac{\partial T}{\partial E} \right)_i \end{bmatrix} \quad (20)$$

$\Delta m$ ,  $\Delta n$ ,  $\Delta p$ ,  $\Delta A$  and  $\Delta E$  values can be obtained by solving eqn. (17). The coefficients in the above equation containing  $T$  are calculated from eqn. (2). The calculation procedure involves the evaluation of two integrals  $F$  and  $G$  as shown in eqn. (3) by a numerical method such as Gauss quadrature for numerical integration as discussed previously [22]. Partial derivatives of  $T$  with respect to  $m$ ,  $n$ ,  $p$ ,  $A$  and  $E$  are related to  $F$  and  $G$  by the following equations

$$\frac{\partial T}{\partial m} = \frac{\partial F}{\partial m} \bigg/ \frac{\partial G}{\partial T} \quad (21)$$

$$\frac{\partial T}{\partial n} = \frac{\partial F}{\partial n} \bigg/ \frac{\partial G}{\partial T} \quad (22)$$

$$\frac{\partial T}{\partial p} = \frac{\partial F}{\partial p} \bigg/ \frac{\partial G}{\partial T} \quad (23)$$

$$\frac{\partial T}{\partial A} = - \frac{\partial G}{\partial A} \bigg/ \frac{\partial G}{\partial T} \quad (24)$$

$$\frac{\partial T}{\partial E} = - \frac{\partial G}{\partial E} \bigg/ \frac{\partial G}{\partial T} \quad (25)$$

The obtained  $\Delta m$ ,  $\Delta n$ ,  $\Delta p$ ,  $\Delta A$  and  $\Delta E$  values are combined with first set of  $m^0$ ,  $n^0$ ,  $p^0$ ,  $A^0$  and  $E^0$  to give a second set of  $\{m^0, n^0, p^0, A^0, E^0\}$ . The process is repeated until the desired accuracy is acquired.

The above discussed method was tested by the data of a zero-order reaction in solution: the acid-catalyzed iodination of acetone [21]. The original data, which are expressed in  $x$  and  $dx/dt$  where  $x$  is the concentration in  $\text{mol l}^{-1}$ , are converted to  $\alpha$  and  $d\alpha/dt$  by the following transformations

$$\alpha = x/a \quad (26)$$

where  $a$  is the initial concentration

$$\frac{d\alpha}{dT} = \frac{1}{C} \frac{d\alpha}{dt} = \frac{1}{aC} \frac{dx}{dt} \quad (27)$$

The data used for testing are shown in Table 1.

The basic kinetic equations are transformed as follows

$$\frac{dx}{dt} = Ae^{-E/RT}(a-x)^n \quad (28)$$

$$\frac{d\alpha}{dt} = \frac{1}{a} \frac{dx}{dt} = Aa^{n-1}e^{-E/RT}(1-\alpha)^n \quad (29)$$

$$\frac{d\alpha}{dT} = \frac{a}{C} \frac{dx}{dt} = \frac{Aa^{n-1}}{C} e^{-E/RT}(1-\alpha)^n \equiv ke^{-E/RT}(1-\alpha)^n \quad (30)$$

$$\ln\left(\frac{d\alpha}{dT}\right) = \ln k - \frac{E}{R}\left(\frac{1}{T}\right) + n \ln(1-\alpha) \quad (31)$$

where  $k = Aa^{n-1}/C$  is a characteristic parameter for the reaction discussed.

By the linear least-squares method, we obtained  $k = 1.143 \times 10^{13} \text{ s}^{-1}$ ,  $E = 71.21 \text{ kJ mol}^{-1}$ ,  $n = -0.1172$ . Based on these initial values of the kinetic parameters, the results obtained from the modified differential correction method by minimizing the temperature are shown in Table 2. As seen in

TABLE 1

Acid-catalyzed iodination of acetone in aqueous solution [22]<sup>a</sup>

Time (min)	Temp. (K)	$\alpha$	$d\alpha/dT$ ( $10^{-5} \text{ min}^{-1}$ )	$T_{\text{calc}}$ (K)
35	287.8	0.133	1.34	287.7
40	289.5	0.172	1.60	289.5
45	291.2	0.219	1.92	291.2
50	292.8	0.277	2.27	293.0
55	294.5	0.342	2.68	294.5
60	296.2	0.413	3.35	296.0
65	297.8	0.522	3.89	297.8
70	299.5	0.642	4.75	299.5

<sup>a</sup> Heating rate,  $1^\circ\text{C min}^{-1}$ ; initial concentration of iodine, 0.003833 M.

TABLE 2

Kinetic parameters from the modified DC method. Minimization with respect to temperature

Count	$n$	$k$ ( $10^{13} \text{ s}^{-1}$ )	$E$ ( $\text{kJ mol}^{-1}$ )
0	-0.1172	1.143	71.21
1	0.3748	2.796	96.30
2	0.2595	3.365	96.28
3	0.2584	3.480	96.31
4	0.2586	3.964	96.32
5	0.2586	3.494	96.32
6	0.2584	3.488	96.32
7	0.2584	3.488	96.32

Table 2, the values of  $n$  and  $E$  are 0.26 and 96.3 kJ mol<sup>-1</sup>, respectively. The theoretical value of  $n$  is 0 and the accepted value of  $E$  is 81.6 kJ mol<sup>-1</sup>. The calculated values of temperature at the corresponding values of  $\alpha$  are listed in the last column of Table 1. It is seen that they are in excellent agreement with the experimental values.

*Modification II. Minimization with respect to kinetic equations in differential form*

Recalling eqn. (30)

$$\frac{d\alpha}{dT} = ke^{-E/RT}(1 - \alpha)^n \quad (30)$$

let

$$f_i = \frac{d\alpha_i}{dT} \quad (32)$$

which can be determined from the experiment, as shown in Table 1, and let

$$g_i = ke^{-E/RT}(1 - \alpha_i)^n \quad (33)$$

Apply the Taylor expansion and neglect the terms in higher powers of  $\Delta k$ ,  $\Delta E$  and  $\Delta n$ , we get

$$g_i = g_i^0 + \frac{\partial g_i^0}{\partial k} \Delta k + \frac{\partial g_i^0}{\partial E} \Delta E + \frac{\partial g_i^0}{\partial n} \Delta n \quad (34)$$

where  $g_i^0$  is the calculated value based on the approximate parameters of  $k$ ,  $E$  and  $n$  from the linear least-squares method. The best set of parameters must be those which would make the following sum of least-squares difference

$$S = \sum \left[ f_i - \left( g_i^0 + \frac{\partial g_i^0}{\partial k} \Delta k + \frac{\partial g_i^0}{\partial E} \Delta E + \frac{\partial g_i^0}{\partial n} \Delta n \right) \right]^2 \quad (35)$$

a minimum. This requires

$$\frac{\partial S}{\partial \Delta k} = 0; \quad \frac{\partial S}{\partial \Delta E} = 0; \quad \frac{\partial S}{\partial \Delta n} = 0$$

and leads to three equations which are linear to the differential corrections,  $\Delta k$ ,  $\Delta E$  and  $\Delta n$ . These three equations can be expressed in the following form

$$\begin{bmatrix} \sum \left( \frac{\partial g_i}{\partial k} \right)^2 & \sum \left( \frac{\partial g_i}{\partial E} \right) \left( \frac{\partial g_i}{\partial k} \right) & \sum \left( \frac{\partial g_i}{\partial n} \right) \left( \frac{\partial g_i}{\partial k} \right) \\ \sum \left( \frac{\partial g_i}{\partial k} \right) \left( \frac{\partial g_i}{\partial E} \right) & \sum \left( \frac{\partial g_i}{\partial E} \right)^2 & \sum \left( \frac{\partial g_i}{\partial n} \right) \left( \frac{\partial g_i}{\partial E} \right) \\ \sum \left( \frac{\partial g_i}{\partial k} \right) \left( \frac{\partial g_i}{\partial n} \right) & \sum \left( \frac{\partial g_i}{\partial E} \right) \left( \frac{\partial g_i}{\partial n} \right) & \sum \left( \frac{\partial g_i}{\partial n} \right)^2 \end{bmatrix} \begin{bmatrix} \Delta k \\ \Delta E \\ \Delta n \end{bmatrix} = \begin{bmatrix} \sum (f_i - g_i^0) \frac{\partial g_i}{\partial k} \\ \sum (f_i - g_i^0) \frac{\partial g_i}{\partial E} \\ \sum (f_i - g_i^0) \frac{\partial g_i}{\partial n} \end{bmatrix} \quad (36)$$

TABLE 3

Kinetic parameters from the modified DC method. Minimization with respect to kinetic equations in differential form

Count	$n$	$k$ ( $10^{13} \text{ s}^{-1}$ )	$E$ ( $\text{kJ mol}^{-1}$ )
0	-0.1172	1.143	71.21
1	-0.0773	2.641	73.85
2	-0.0769	3.423	73.89
3	-0.0769	3.425	73.89
4	-0.0769	3.426	73.89
5	-0.0769	3.425	73.89
6	-0.0769	3.425	73.89
7	-0.0769	3.425	73.89

$\Delta k$ ,  $\Delta E$  and  $\Delta n$  values can be obtained by solving eqn. (36).  $f_i$  is determined experimentally, and the partial derivatives of  $g_i$  with respect to  $k$ ,  $E$  and  $n$  are obtained by differentiating eqn. (33). The obtained  $\Delta k$ ,  $\Delta E$  and  $\Delta n$  values are combined with the first set of  $k^0$ ,  $E^0$  and  $n^0$  to give a second set of  $\{k, E, n\}$ . The process is repeated until the values of  $k$ ,  $n$  and  $E$  converge.

The validity of this treatment was also tested by the data of the zero-order reaction of acid-catalyzed iodination of acetone. Results obtained from the differential correction method by minimizing the kinetic quantities in differential form are shown in Table 3. The values of  $n$  and  $E$  are  $-0.08$  and  $73.9 \text{ kJ mol}^{-1}$ , respectively, closer to the theoretical value of  $n$  and the accepted value of  $E$ . This method has the merit of simplicity. The tedious procedure of numerical integration of  $F$  and  $G$  is avoided.

In conclusion, two modifications to the combined numerical differential correction method for evaluating kinetic parameters from thermogravimetric data are proposed. The first modification is based on the minimization of the sum-of-squares difference between the observed and calculated temperatures and the other is based on a non-linear least-squares treatment of the kinetic expressions in differential form. Both methods were tested by the experimental data of acid-catalyzed iodination of acetone and the results were satisfactory.

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