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EVALUATION OF KINETIC PARAMETERS FROM THERMOGRAVIMETRIC CURVES

PART I. COMBINED NUMERICAL METHOD

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ABSTRACT

A new method is proposed to evaluate kinetic parameters from thermogravimetric traces. The method consists of two steps. α, T and $d\alpha/dT$ values are first employed to estimate kinetic parameters by linear least squares fitting, using the five types of mechanism for solid phase reactions suggested by Šesták. From the different sets of parameters thus obtained, the most probable mechanism type is decided. The resultant parameters for the chosen type of mechanism may further be improved by differential correction method, if necessary, using the more accurate data of α and T. The proposed method was tested with artificial data and the data for the thermal dehydration of gypsum by Šesták et al. The results were very satisfactory.

INTRODUCTION

Many methods and modifications have been proposed to evaluate kinetic parameters of solid phase reactions from thermogravimetric curves[1–19]. Most of them employ the simplest type of reaction mechanism, $f(\alpha) = (1-\alpha)^n$ and determine the value of n by the trial-and-error method. Only a few can determine E and n directly. Recently, Gay[20] proposed a numerical quadrature method which can also be applied to such cases. In reality, the mechanisms of solid phase reactions are very complicated. According to Šesták[21] there are five types of mechanisms which have already been discovered. A general formula is given:

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

where α 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 mechanisms are m, n, p, mn and np. In this paper an attempt is made to analyse thermogravimetric data according to these five types. The linear least squares (LLS) method by Gay is first employed to find out the correct type of mechanism. The kinetic parameters thus obtained are improved by applying the differential correction (DC) technique.

Take the most common mechanism type as an example:

$$\frac{d\alpha}{dt}=k\alpha^m(1-\alpha)^n \tag{2}$$

Replace k by the Arrhenius equation

$$\frac{d\alpha}{dt}=Ae^{-E/RT}\alpha^m(1-\alpha)^n \tag{3}$$

Take logarithm

$$\ln\frac{d\alpha}{dt}=\ln A-\frac{E}{R}\left(\frac{1}{T}\right)+m\ln\alpha+n\ln(1-\alpha) \tag{4}$$

Equation (4) may be written in the following form

$$y=p_1+p_2x+p_3z+p_4u \tag{5}$$

where y, x, z and u are variables representing $\ln d\alpha/dt$, $1/T$, $\ln\alpha$ and $\ln(1-\alpha)$, respectively and the p's are constants which contain four parameters, A, E, m and n. The sum of squares error S is given by

$$S=\sum_{i=1}^{n}(y_i-p_1-p_2x_i-p_3z_i-p_4u_i)^2 \tag{6}$$

where the subscript i designates the ith data point and n is the number of data points taken. The best set of parameters should meet the following conditions:

$$\frac{\partial S}{\partial p_1}=-\Sigma 2(y_i-p_1-p_2x_i-p_3z_i-p_4u_i)=0 \tag{7}$$

$$\frac{\partial S}{\partial p_2}=-\Sigma 2x_i(y_i-p_1-p_2x_i-p_3z_i-p_4u_i)=0 \tag{8}$$

$$\frac{\partial S}{\partial p_3}=-\Sigma 2z_i(y_i-p_1-p_2x_i-p_3z_i-p_4u_i)=0 \tag{9}$$

$$\frac{\partial S}{\partial p_4}=-\Sigma 2u_i(y_i-p_1-p_2x_i-p_3z_i-p_4u_i)=0 \tag{10}$$

All the summations are taken from 1 to n. From the above equations, the following expressions are obtained:

$$\Sigma y_i=np_1+p_2\Sigma x_i+p_3\Sigma z_i+p_4\Sigma u_i \tag{11}$$

$$\Sigma x_iy_i=p_1\Sigma x_i+p_2\Sigma x_i^2+p_3\Sigma x_iz_i+p_4\Sigma x_iu_i \tag{12}$$

$$\Sigma z_i y_i = p_1 \Sigma z_i + p_2 \Sigma z_i x_i + p_3 \Sigma z_i^2 + p_4 \Sigma z_i u_i \tag{13}$$

$$\Sigma u_i y_i = p_1 \Sigma u_i + p_2 \Sigma u_i x_i + p_3 \Sigma u_i z_i + p_4 \Sigma u_i^2 \tag{14}$$

The four constants p_1, p_3, p_2 and p_4 can be obtained by solving these normal equations simultaneously, and the four parameters, A, E, m and n can, in turn, be calculated. By a similar manner, kinetic parameters for the other four types of mechanism can be evaluated. The correctness of the assumed mechanism type is judged from the rationality of the deduced parameters. For instance, Šesták et al.[22] claimed that the value of A for simple decomposition reactions should not differ from 10^{12} by more than two orders of magnitude. Once the correct mechanism type is determined, the values of the parameters obtained above could further be improved, because in the above method, $\mathrm{d}\alpha/\mathrm{d}t$ data are employed which are secondary data; they are less accurate than the data of α and T. A least squares method based on α and T is, therefore, suggested to improve the above deduced kinetic parameters. The principle is as follows:

Start from a general equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\,\mathrm{e}^{-E/RT}\,\mathrm{f}(\alpha) \tag{15}$$

The meanings of all the symbols have been defined previously. Substituting $\mathrm{d}t = \mathrm{d}T/a$, rearranging and integrate between limits, eqn (15) becomes

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \frac{A}{a}\int_0^{T} \mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{16}$$

where a is the heating rate. The sum of the squares error is, then, defined by

$$S = \Sigma\left[\int_0^{\alpha_i} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} - \frac{A}{a}\int_0^{T_i} \mathrm{e}^{-E/RT}\,\mathrm{d}T\right]^2 \tag{17}$$

Since it has been determined above that the reaction mechanism is of m, n type, then $\mathrm{f}(\alpha)$ is a function of α, m and n, and $\int_0^{\alpha} \mathrm{d}\alpha/\mathrm{f}(\alpha)$ should also be a function of α, m and n. Let

$$\int_0^{\alpha_i} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = F(\alpha_i, m, n) = F_i \tag{18}$$

and

$$\frac{A}{a}\int_0^{T_i} \mathrm{e}^{-E/RT}\,\mathrm{d}T = G(T_i, A, E) = G_i \tag{19}$$

Equation (17) becomes

$$S = \Sigma(F_i - G_i)^2 \tag{20}$$

The necessary conditions for this sum to be a minimum are: $\partial S/\partial m = 0$, $\partial S/\partial n = 0$, $\partial S/\partial A = 0$ and $\partial S/\partial E = 0$. Thus four normal equations can be established. However, these normal equations are non-linear; they are difficult to be solved simultaneously. The differential correction technique is, therefore, introduced.

Let m°, n°, A° and E° be the approximate value of these parameters derived from LLS method described above; Δm, Δn, ΔA and ΔE be the corrections that must be applied in order to achieve the condition of "best fit", then

$$m = m^\circ + \Delta m \tag{21}$$

$$n = n^\circ + \Delta n \tag{22}$$

$$A = A^\circ + \Delta A \tag{23}$$

$$E = E^\circ + \Delta E \tag{24}$$

According to Taylor's expansion

$$F(\alpha_i, m, n) = F_i^\circ + (Fm)_i \Delta m + (Fn)_i \Delta n + (Fm)_i^2 (\Delta n)^2 + (Fn)_i^2 (\Delta n)^2 + \ldots \tag{25}$$

$$G(T_i, A, E) = G_i^\circ + (GA)_i \Delta A + (GE)_i \Delta E + (GA)_i^2 (\Delta A)^2 + (GE)_i^2 (\Delta E)^2 + \ldots \tag{26}$$

where $F^\circ = F(\alpha_i, m^\circ, n^\circ)$, $G^\circ = G(T_i, A^\circ, E^\circ)$, $(Fm)_i$ represents a partial derivative of F with respect to m, $(Fm)_i^2$ represents the second partial derivative of F with respect to m, then substitute in the values of m° and n°. Other functions assume a similar meaning. If the higher powers in Δm, Δn, ΔA and ΔE are neglected, eqn (20) becomes

$$\begin{aligned} S &= \Sigma[F(\alpha_i, m, n) - G(T_i, A, E)]^2 \\ &= \Sigma[F_i^\circ - G_i^\circ + (Fm)_i \Delta m + (Fn)_i \Delta n - (GA)_i \Delta A - (GE)_i \Delta E]^2 \end{aligned} \tag{27}$$

Now the problem has been reduced to find suitable values of Δm, Δn, ΔA and ΔE so as to make S a minimum. The necessary conditions are

$$\frac{\partial S}{\partial \Delta m} = 2\Sigma[F_i^\circ - G_i^\circ + (Fm)_i \Delta m + (Fn)_i \Delta n - (GA)_i \Delta A - (GE)_i \Delta E](Fm)_i = 0 \tag{28}$$

$$\frac{\partial S}{\partial \Delta n} = 2\Sigma[F_i^\circ - G_i^\circ + (Fm)_i \Delta m + (Fn)_i \Delta n - (GA)_i \Delta A - (GE)_i \Delta E](Fn)_i = 0 \tag{29}$$

$$\frac{\partial S}{\partial \Delta A} = 2\Sigma[F_i^\circ - G_i^\circ + (Fm)_i \Delta m + (Fn)_i \Delta n - (GA)_i \Delta A - (GE)_i \Delta E](GA)_i = 0 \tag{30}$$

$$\frac{\partial S}{\partial \Delta E} = 2\Sigma[F_i^\circ - G_i^\circ + (Fm)_i \Delta m + (Fn)_i \Delta n - (GA)_i \Delta A - (GE)_i \Delta E](GE)_i = 0 \tag{31}$$

These equations lead to the following expressions

$$\begin{aligned} &\Sigma(F_i^\circ - G_i^\circ)(Fm)_i + \Delta m \Sigma(Fm)_i^2 + \Delta n \Sigma(Fm)_i (Fn)_i - \Delta A \Sigma(Fm)_i (GA)_i - \\ &\qquad - \Delta E \Sigma(Fm)_i (GE)_i = 0 \end{aligned} \tag{32}$$

$$\Sigma(F_i^\circ - G_i^\circ)\,(Fn)_i + \Delta m\Sigma(Fn)_i(Fm)_i + \Delta n\Sigma(Fn)_i^2 - \Delta A\Sigma(Fn)_i(GA)_i - \\ - \Delta E\Sigma(Fn)_i(GE)_i = 0 \qquad (33)$$

$$\Sigma(F_i^\circ - G_i^\circ)\,(GA)_i + \Delta m\Sigma(GA)_i(Fm)_i + \Delta n\Sigma(GA)_i(Fn)_i - \Delta A\Sigma(GA)_i^2 - \\ - \Delta E\Sigma(GA)_i(GE)_i = 0 \qquad (34)$$

$$\Sigma(F_i^\circ - G_i^\circ)\,(GE)_i + \Delta m\Sigma(GE)_i(Fm)_i + \Delta n\Sigma(GE)_i(Fn)_i - \Delta A\Sigma(GE)_i(GA)_i - \\ - \Delta E\Sigma(GE)_i^2 = 0 \qquad (35)$$

These equations are linear in Δm, Δn, ΔA and ΔE, and can readily be solved if all the coefficients are evaluated. F°, G°, $(Fm)_i$, $(Fn)_i$, $(GA)_i$ and $(GE)_i$ all involve integration. Because there is no exact integrand for the G function and no common form for the F function, the values of these definite integrals are evaluated by numerical integration based on Gauss quadrature. A detailed method can be found in any standard text book of numerical analysis. A brief procedure is presented in Appendix 1. When all these values have been evaluated and substituted into eqns (32) to (35), they can be solved to get Δm, Δn, ΔA and ΔE values. Because the series from Taylor's expansion has been truncated by neglecting the second and higher order terms, solution from above equations cannot be expected to give, at once, the best values of Δm, Δn, ΔA and ΔE. The values thus obtained, are combined with the originally assumed m°, n°, A° and E° values. The procedure is repeated to obtain another set of corrections until the desired accuracy is acquired. Similar treatment applies to other types of mechanisms.

TESTING OF THE METHOD

The validity of the present method was tested by artificial data and the thermogravimetric data of dehydration of gypsum by Šesták et al.[23]. Two sets of artificial data were tested; both yielded satisfactory results. However, only one set is presented here. The data were generated using Newton and Raphson's method and are shown in Table 1. Kinetic parameters and the conditions used were: $A = 5.000 \times 10^{11}$ sec^{-1}, $E = 26.000$ kcal mol^{-1}, $a = 3$°C min^{-1}, $f(\alpha) = (1-\alpha)^{1/3}[-\ln(1-\alpha)]^{-1}$. Results obtained by LLS method are shown in Table 2. All the calculations were done by an ICL 1904A computer. For the sake of simplicity, only two types of mechanism were tested. From the rationality of A values, it can be concluded that the *np* type of mechanism is preferable. Results obtained by DC procedure are shown in Table 3. Parameters in count 0 were taken from the LLS method. After three counts, the changes of parameters were very small, and the iterating procedure was terminated. The resultant parameters agree excellently with the assumed values.

The thermogravimetric data for dehydration of gypsum by Šesták et al. have also been used by Vachuska and Vobaril[18] to verify their differential-differential procedure and will not be reproduced here. Results obtained by the LLS method are

TABLE 1

ARTIFICIAL DATA FOR $A = 5.000 \times 10^{11}$ sec^{-1}, $E = 26.000$ kcal mol^{-1}
$f(\alpha) = (1-\alpha)^{1/3}[-\ln(1-\alpha)]^{-1}$, $a = 3$°C min^{-1}

α (10^{-3})	T (K)	$d\alpha/dt$ (10^{-3} sec^{-1})	α (10^{-3})	T (K)	$d\alpha/dt$ (10^{-3} sec^{-1})
10	313.045	0.70	510	385.028	19.2
30	329.666	1.88	530	386.058	19.6
50	338.047	2.96	550	387.067	20.0
70	343.833	3.99	570	388.061	20.3
90	348.311	4.97	590	389.039	20.6
110	351.991	5.92	610	390.004	20.8
130	355.134	6.83	630	390.959	21.0
150	357.888	7.71	650	391.906	21.2
170	360.349	8.56	670	392.846	21.3
190	362.578	9.39	690	393.782	21.4
210	364.622	10.2	710	394.715	21.4
230	366.513	11.0	730	395.649	21.4
250	368.277	11.7	750	396.586	21.3
270	369.933	12.4	770	397.529	21.1
290	371.497	13.1	790	398.481	20.9
310	372.980	13.8	810	399.446	20.5
330	374.393	14.5	830	400.430	20.1
350	375.744	15.1	850	401.438	19.6
370	377.042	15.7	870	402.478	18.9
390	378.291	16.3	890	403.563	18.0
410	379.497	16.9	910	404.708	16.9
430	380.665	17.4	930	405.940	15.5
450	381.799	17.9	950	407.307	13.7
470	382.902	18.4	970	408.930	11.2
490	383.977	18.8	990	411.077	7.01

TABLE 2

RESULTS FROM LLS PROCEDURE FOR ARTIFICIAL DATA

$f(\alpha)$	A (sec^{-1})	E (kcal mol^{-1})	n	m	p
$(1-\alpha)^n[-\ln(1-\alpha)]^p$	4.157×10^{11}	25.855	0.3356		−0.9895
$(1-\alpha)^n\alpha^m$	43.55	7.765	0.4823	0.3359	

TABLE 3

RESULTS FROM DC PROCEDURE FOR ARTIFICIAL DATA

Assume $f(\alpha) = (1-\alpha)^n[-\ln(1-\alpha)]^p$.

Count	A (10^{11} sec^{-1})	E (kcal mol^{-1})	n	p
0	4.157	25.855	0.3356	−0.9895
1	4.927	26.000	0.3333	−1.0000
2	4.999	26.000	0.3334	−1.0000
3	4.999	26.000	0.3333	−1.0000

TABLE 4

RESULTS FROM LLS PROCEDURE FOR DEHYDRATION OF GYPSUM

$f(\alpha)$	A (sec^{-1})	E (kcal mol^{-1})	n	m	p
α^m	4.259×10^{-25}	-43.862		2.5688	
$(1-\alpha)^n$	5.758×10^{11}	26.820	0.9998		
$[-\ln(1-\alpha)]^p$	4.964×10^{5}	3.414×10^{4}			-1.202×10^{3}
$\alpha^m(1-\alpha)^n$	9.665×10^{12}	29.152	1.033	-0.085	
$(1-\alpha)^n[-\ln(1-\alpha)]^p$	2.467×10^{-9}	-11.877	1.003		1.3645

TABLE 5

RESULTS FROM DC PROCEDURE FOR DEHYDRATION OF GYPSUM

Assume $f(\alpha) = (1-\alpha)^n$.

Count	A (sec^{-1})	E (kcal mol^{-1})	n
0	5.758×10^{11}	26.820	0.9998
1	5.807×10^{11}	26.828	1.0004
2	5.808×10^{11}	26.828	1.0004

TABLE 6

COMPARISON OF RESULTS OBTAINED FROM THREE METHODS FOR DEHYDRATION OF GYPSUM

Method	A (10^{11} sec^{-1})	E (kcal mol^{-1})	n	S
Šesták et al.	5.789	26.82	0.9392	1.6×10^{-2}
Vachuska and Voboril	5.754	26.817	1.000	2.1×10^{-4}
Present	5.808	26.828	1.0004	3.0×10^{-6}

shown in Table 4. All the five types of mechanism were tried. The rationality of A values suggests the n type of mechanism. Results obtained by the DC method are shown in Table 5. Only two iterating procedures were required. It is concluded that the thermal dehydration of gypsum follows the phase boundary reaction mechanism of first order, with an activation energy of 26.8 kcal mol^{-1} and a frequency factor of 5.8×10^{11} sec^{-1}. The results agree excellently with those obtained by Šesták et al. and by Vachuska and Vobaril as shown in Table 6. However, the present method gives the smallest sum of squares error.

It is seen, from the above tests, that the proposed procedure is satisfactory for determining reaction mechanisms and evaluating kinetic parameters of solid phase reactions. Judging from the two sets of data tested, it would seem that the crumblesome procedure of differential correction does not play any important role in the proposed method; kinetic parameters obtained by applying the LLS procedure alone are sufficiently accurate. But, as will be seen in part II of this paper, the DC procedure does make some contribution to the accuracy of parameter evaluation. The reason that the DC procedure does not make any significant improvement of accuracy in the present two cases is due to very high accuracy of the $d\alpha/dt$ data.

APPENDIX 1

GAUSS QUADRATURE FOR NUMERICAL INTEGRATION

Suppose we want to integrate any function $f(x)$ between two limits a and b

$$I = \int_a^b f(x)dx \tag{36}$$

it is first transformed into another definite integral with limits between -1 to 1. This is done by introducing a new variable u such that

$$x = \tfrac{1}{2}(b-a)u + \tfrac{1}{2}(b+a) \tag{37}$$

and

$$dx = \tfrac{1}{2}(b-a)du \tag{38}$$

It can be seen that at $x = a$,

$$u = \frac{2a-b-a}{b-a} = -1 \tag{39}$$

and at $x = b$,

$$u = \frac{2b-b-a}{b-a} = 1 \tag{40}$$

Hence eqn (36) becomes

$$I = \frac{(b-a)}{2}\int_{-1}^{1} f[\tfrac{1}{2}(b-a)u + \tfrac{1}{2}(b+a)]du \tag{41}$$

Such a definite integral could be approxiated by a properly weighed sum of any number of particular values of v_j suitably distributed between -1 to 1. If we take sixteen terms, then eqn (41) becomes

$$I = \frac{b-a}{2}\sum_{j=1}^{16} f[\tfrac{1}{2}(b-a)v_j + \tfrac{1}{2}(b+a)]g_j \tag{42}$$

where v_j is the discrete abscissa and g_j is the corresponding weight coefficient. The corresponding sixteen v_j ad g_j values are listed in Appendix 2[24].

As an illustrative example, let us consider the evaluation of the term $(GE)_i$

Since

$$G_i = \frac{A}{a}\int_0^{T_i} \mathrm{e}^{-E/RT}\,\mathrm{d}t \tag{43}$$

then,

$$\begin{aligned}(GE)_i &= \frac{\partial G_i}{\partial E} = \frac{\partial}{\partial E}\left[\frac{A}{a}\int_0^{T_i} \mathrm{e}^{-E/RT}\,\mathrm{d}T\right] \\ &= \frac{A}{a}\int_0^{T_i}\left[\frac{\partial}{\partial E}(\mathrm{e}^{-E/RT})\right]\mathrm{d}T \\ &= -\frac{A}{aR}\int_0^{T_i}\frac{1}{T}\mathrm{e}^{-E/RT}\,\mathrm{d}T \end{aligned} \tag{44}$$

In this case $a = 0$, $b = T_i$, substitute into eqn (41), eqn (44) becomes

$$\begin{aligned}(GE)_i &= -\frac{A}{aR}\frac{T_i}{2}\int_{-1}^{1}\left[\frac{1}{\frac{T_i}{2}u + \frac{T_i}{2}}\mathrm{e}^{-E/R(T_i/2u+T_i/2)}\right]\mathrm{d}u \\ &= -\frac{AT_i}{aR}\int_{-1}^{1}\left[\frac{1}{T_i(u+1)}\mathrm{e}^{-2E/RT_i(u+1)}\right]\mathrm{d}u \end{aligned} \tag{45}$$

Substitute into eqn (42), we have

$$(GE)_i = -\frac{AT_i}{aR}\sum_{j=1}^{16}\frac{g_j}{T_i(v_j+1)}\mathrm{e}^{-2E/RT_i(v_j+1)} \tag{46}$$

Substituting the corresponding values of v_j and g_j from Appendix 2, we have

$$\begin{aligned}(GE)_i = -\frac{AT_i}{aR}\Bigg[&\frac{0.0271524594}{1.9894009350\,T_i}\mathrm{e}^{-2E/1.9894009350\,RT_i} \\ &+ \frac{0.0622535239}{1.9445750231\,T_i}\mathrm{e}^{-2E/1.9445750231\,RT_i} \\ &+ \text{---} \\ &+ \frac{0.0271524594}{0.0105000650\,T_i}\mathrm{e}^{-2E/0.0105000650\,RT_i}\Bigg]\end{aligned} \tag{47}$$

The other terms can be evaluated in a similar way. There are n such (GE) values and n values of other terms, where n is the number of experimental points.

APPENDIX 2

GAUSS'S QUADRATURE COEFFICIENTS FOR $n = 16$

j	v_j	g_j
1	0.9894009350	0.0271524594
2	0.9445750231	0.0622535239
3	0.8656312024	0.0951585117
4	0.7554044084	0.1246289713
5	0.6178762444	0.1495959888
6	0.4580167777	0.1691565194
7	0.2816035508	0.1826034150
8	0.0950125098	0.1894506105
9	−0.0950125098	0.1894506105
10	−0.2816035508	0.1826034150
11	−0.4580167777	0.1691565194
12	−0.6178762444	0.1495959888
13	−0.7554044084	0.1246289713
14	−0.8656312024	0.0951585117
15	−0.9445750231	0.0622535239
16	−0.9894009350	0.0271524594

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