Journal of Thermal Analysis, Vol. 20 (1981) 233—243

A TESTING OF SOME DYNAMIC KINETIC EQUATIONS

PART IV. ARTIFICIAL DATA

David T. Y. Chen and Kai-Wing Lai

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong

(Received June 3, 1980)

Artificial thermogravimetric data relating to the five possible types of mechanisms proposed by Sestak and Berggren were synthesized to test four dynamic kinetic methods: the Horowitz and Metzger, Freeman and Carroll, Coats and Redfern, and Linear Least Squares Fitting methods. It was found that the Linear Least Squares Fitting method is the most satisfactory.

Determination of kinetic parameters by a dynamic method has several advantages over the isothermal method [1]. As the following integrand

$$G = \int_0^T \exp(-E/RT)\,\mathrm{d}T \tag{1}$$

has no exact solution, we have to accept an approximate answer. Many authors have employed different approaches to the approximation. Among them, Freeman and Carroll's method and Coats and Redfern's method are well known and have been tested by several authors [2]. Chen and Fong [3] used their kinetic data relating to three different orders of reactions in solution to test these two methods, plus Horowitz and Metzger's method and the one proposed by Achar et al. [4]. Their conclusion favours Freeman and Carroll's method. All the four tested methods assume that $f(\alpha) = (1 - \alpha)^n$. In reality, the mechanisms of solid-phase reactions are much complicated. According to Sestak and Berggren [5] there are five possible types of solid-phase reaction mechanisms. It is obvious that the above-mentioned testings are not adequate enough. In this paper artificial thermoanalytical data for all the five possible types of mechanism are synthesized to test the three methods tested by Chen and Fong, plus the LLSF method proposed by them [6]. During the preparation of this manuscript, an exhaustive paper on testing equations was published by Dankiewicz and Wieczorek-Ciurowa [7]. Fourteen equations, including DTA methods and several-curve methods, were tested using experimental data on the dehydration of syngenite. Their results favour the method of Šatava and Škvara [8].

Synthesis of thermoanalytical data

After the separation of variables, a general equation for dynamic kinetic process may be written as

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\Phi}\int_0^T \exp(-E/RT)\,dT \tag{2}$$

where α is the fraction reacted at temperature T, and A, E and Φ are the frequency factor, activation energy and heating rate, respectively. Equation (2) may be symbolized as

$$F = G. \tag{3}$$

For a given reaction mechanism with assumed values of m, n and/or p, F was computed by Gauss' Quadrature [9], and G was computed by Newton–Raphson's method [9]. Theoretical α, T and $d\alpha/dT$ data for five possible mechanisms were calculated with A, Φ and E assumed to be 5.0×10^{15}, 5°/min and 210.0 kJ per mole, respectively. These five possible mechanisms are:

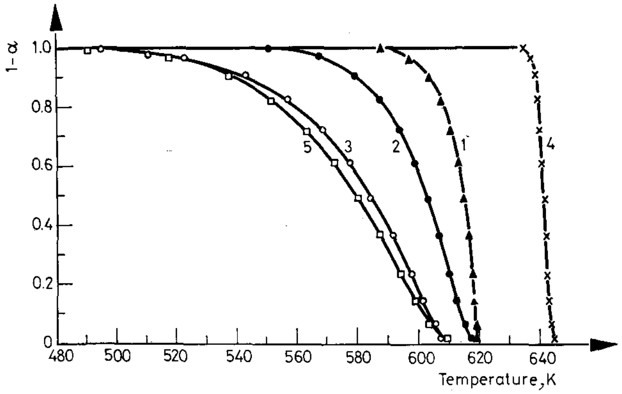

Fig. 1. Plot of $(1-\alpha)$ vs. T for five sets of artificial data. (1) $f(\alpha) = \alpha^{1/2}$, (2) $f(\alpha) = (1-\alpha)^{1/2}$ (3) $f(\alpha) = [-\ln(1-\alpha)]^{-1}$, (4) $f(\alpha) = \alpha(1-\alpha)$, (5) $f(\alpha) = (1-\alpha)^{1/3}[-\ln(1-\alpha)]^{-1}$

(1) $f(\alpha) = \alpha^m$, $m = 0.5$; the reaction is controlled by nucleation according to the power law.

(2) $f(\alpha) = (1-\alpha)^n$, $n = 0.5$; the reaction is controlled by two-dimensional movement of the phase boundary.

(3) $f(\alpha) = [-\ln(1-\alpha)]^p$, $p = -1$; the reaction is controlled by diffusion with two-dimensional transport.

(4) $f(\alpha) = \alpha^m(1-\alpha)^n$, $m = 1$, $n = 1$; the reaction is controlled by nucleation, followed by linear growth of nuclei, with branching nuclei interacting during their growth.

(5) $f(\alpha) = (1-\alpha)^n[-\ln(1-\alpha)]^p$, $n = \frac{1}{3}$, $p = -1$; the reaction is controlled by diffusion with three-dimensional transport in a sphere (Jander's equation).

Plots of $(1-\alpha)$ vs. T for these five sets of artificial data are shown in Fig. 1.

Testing of methods

1. *Horowitz and Metzger's method* [10]

The variable T is converted to θ by $\theta = T - T_m$, where T_m is the temperature at which the rate is a maximum. $f(\alpha)$ is assumed to be $(1-\alpha)^n$. The value of n is estimated from α_m, the fraction reacted at T_m. If $1 - \alpha_m = 1/e$, then $n = 1$, and the following equation is used to estimate the energy of activation:

$$\ln\,[-\ln\,(1-\alpha) = \frac{E}{RT_m^2}\,\theta\,. \tag{4}$$

A plot of $\ln\,[-\ln\,(1-\alpha)]$ *vs.* θ should be a straight line with slope E/RT_m^2. If $1 - \alpha_m \neq \frac{1}{e}$, the following equation is used to find n:

$$1 - \alpha_m = n^{1/(1-n)} \tag{5}$$

and the following linear relationship is used to evaluate E:

$$\ln \frac{1-(1-\alpha)^{(1-n)}}{1-n} = \frac{E}{RT_m^2}\,\theta\,. \tag{6}$$

A plot of the left hand side vs. θ should give a straight line with slope E/RT_m^2. In the present case, Eq. (6) was employed.

An inspection of Fig. 1 (and also the calculated $\frac{d\alpha}{dt}$ values, not given in this paper) shows that the *m*-mechanism has no inflection point, and therefore no T_m. This fact can easily be understood. Since $d\alpha/dt = k_T\alpha^m$, α increases with t, and so should α^m. k_T increases with T and, in turn, with t. Therefore, their product should also increase with t or T, and no maximum exists in the $d\alpha/dt$ *vs.* T curve. Hence, this set of data can not be treated by Horowitz and Metzger's method. Results of treatment of the other sets of data are shown in Fig. 2; kinetic parameters derived are tabulated in Table 1.

It is seen from Fig. 2 that the four lines are quite linear within the range plotted; deviations occur with large values of θ. An *m*, *n*-type of mechanism gives a line

Table 1

Kinetic parameters derived from Horowitz and Metzger's method

True mechanism	α_m	T_m, K	Estimated, n	E, kJ · M^{-1}
$f(\alpha) = (1-\alpha)^{0.5}$	0.76	609.8°	0.47	217.2
$f(\alpha) = [-\ln\,(1-\alpha)]^{-1}$	0.81	599.8	0.33	114.6
$f(\alpha) = \alpha(1-\alpha)$	0.54	640.8	1.63	2478.0
$f(\alpha) = (1-\alpha)^{1/3}[-\ln\,(1-\alpha)]^{-1}$	0.70	591.1	0.69	119.0

of very good linearity. Thus, Horowitz and Metzger's method will lead to a false result. With a true n-type of mechanism, however, the result is not bad.

2. *Freeman and Carrol's method* [11]

Their final equation is

$$\frac{\Delta \ln (\mathrm{d}\alpha/\mathrm{d}t)}{\Delta \ln (1-\alpha)} = n - \frac{E}{R}\frac{\Delta (1/T)}{\Delta \ln (1-\alpha)}\,. \tag{7}$$

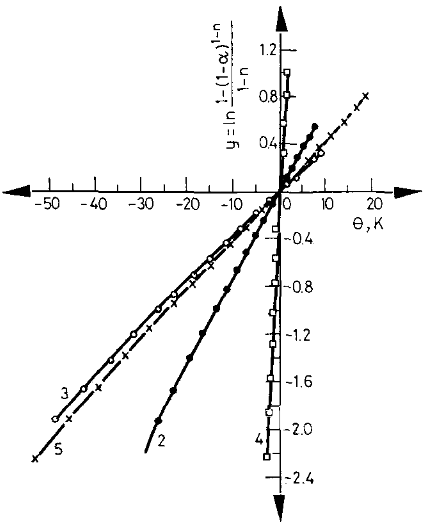

Fig. 2. Horowitz and Metzger's treatment for five sets of artificial data. (2) $f(\alpha) = (1-\alpha)^{1/2}$, (3) $f(\alpha) = [-\ln(1-\alpha)]^{-1}$, (4) $f(\alpha) = \alpha(1-\alpha)$, (5) $f(\alpha) = (1-\alpha)^{1/3}[-\ln(1-\alpha)]^{-1}$

A plot of $\frac{\Delta \ln (\mathrm{d}\alpha/\mathrm{d}t)}{\Delta \ln (1-\alpha)}$ *vs.* $\frac{\Delta (1/T)}{\Delta \ln (1-\alpha)}$ should result in a straight line with slope $-E/R$ and intercept n. Results of treatment of the five sets of artificial data are shown in Fig. 3; kinetic parameters derived are listed in Table 2. Although m-

Table 2

Kinetic parameters derived from Freeman and Carroll's method

True mechanism	Estimated n	E, kJ · M^{-1}
$f(\alpha) = \alpha^{0.5}$	-0.12	424.2
$f(\alpha) = (1-\alpha)^{0.5}$	0.56	210.5
$f(\alpha) = [-\ln(1-\alpha)]^{-1}$	0.39	101.5
$f(\alpha) = \alpha(1-\alpha)$	-1.53	1843.4
$f(\alpha) = (1-\alpha)^{1/3}[-\ln(1-\alpha)]^{-1}$	0.63	101.2

and m, n-types of mechanism yield unreasonable results (negative reaction order), the results given by p- and n, p-types of mechanism can not be considered unreasonable. It is surprising to note that the linearities of p- and n, p-types are even better than for the true mechanism; the activation energy values, however, are not correct. Hence, it must be concluded that Freeman and Carroll's method will also lead to a false result. With the true mechanism, of n-type, the results obtained are satisfactory.

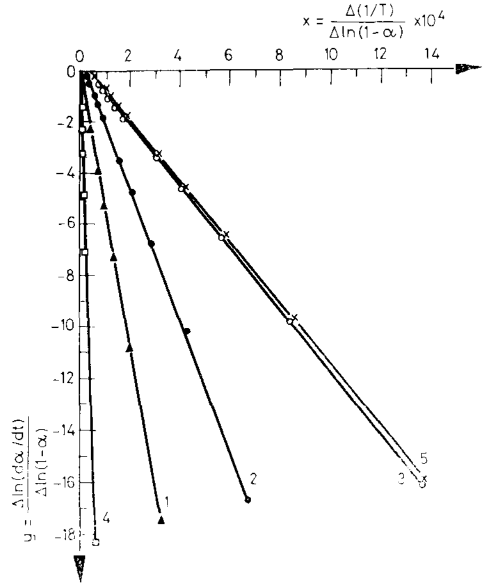

Fig. 3. Freeman and Carroll's treatment for five sets of artificial data. (1) $f(\alpha) = \alpha^{1/2}$, (2) $f(\alpha) = (1 - \alpha)^{1/2}$, (3) $f(\alpha) = [-\ln(1 - \alpha)]^{-1}$, (4) $f(\alpha) = \alpha(1 - \alpha)$, (5) $f(\alpha) = (1 - \alpha)^{1/3}[-\ln(1 - \alpha)]^{-1}$

3. *Coats and Redfern's method* [12]

Assuming an n-type of mechanism, the final equation they obtained for $n \neq 1$, is

$$\ln \frac{1 - (1 - \alpha)^{1-n}}{(1 - n)T^2} = \ln \frac{AR}{\Phi E}\left[1 - 2\left(\frac{RT}{E}\right) + 6\left(\frac{RT}{E}\right)^2 + \ldots\right] - \frac{E}{R}\left(\frac{1}{T}\right). \tag{8}$$

For $n = 1$, it becomes

$$\ln \frac{-\ln(1 - \alpha)}{T^2} = \ln \frac{AR}{\Phi E}\left[1 - 2\left(\frac{RT}{E}\right) + 6\left(\frac{RT}{E}\right)^2 + \ldots\right] - \frac{E}{R}\left(\frac{1}{T}\right). \tag{9}$$

The first terms in the right-hand sides of the above two equations are constant for most values of E and the usual reaction temperature range, i.e. $20 < \frac{E}{RT} < 60$; a plot of either $\ln\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}$ against $\frac{1}{T}$ or, when $n = 1$, $\ln\frac{-\ln(1-\alpha)}{T^2}$ against $\frac{1}{T}$ should give a straight line of slope $-\frac{E}{R}$ for the right value of n.

In order to obtain a more complete idea of probable reaction mechanisms from thermoanalytical data for which $f(\alpha)$ is not restricted to n-type only, integrand F is expressed in a general form

$$F = \int_0^\alpha \frac{d\alpha}{\alpha^m(1-\alpha)^n\,[-\ln(1-\alpha)]^p}\,. \tag{10}$$

Coats and Redfern's equation becomes

$$\ln\left(\frac{F}{T^2}\right) = \ln\frac{AR}{\Phi E}\left[1 - 2\left(\frac{RT}{E}\right) + 6\left(\frac{RT}{E}\right)^2 + \ldots\right] - \frac{E}{R}\left(\frac{1}{T}\right). \tag{11}$$

A trial and error procedure was employed. Values of m, n and p were assigned and F was computed by Gauss' Quadrature method. If the assigned values of m, n and p are the right ones, then a plot of $\ln\left(\frac{F}{T^2}\right)$ *vs.* $\frac{1}{T}$ should result in a straight line with slope $-E/R$.

In accordance with Sestak and Berggren [5], values of the reaction order parameters tried are as follows:

(1) for simple mechanism types, m varies from -1.8 to 0.8, n from 0 to 2.0, and p from -1.8 to 0, all with successive increments of 0.2;

(2) for a combined m, n-type of mechanism, both m and n vary from 0 to 1.0 with successive increments of 0.1;

(3) for a combined n, p-type of mechanism, the following values were tried

(i) $n = 1,\ p = \frac{1}{3}, \frac{1}{2}, \frac{2}{3}, \frac{3}{4}$

(ii) $n = \frac{1}{3}, \frac{2}{3}, p = -1$.

The above three treatments were all applied to the five sets of artificial data. The results obtained are shown in Table 3. In this Table, only those lines with correlation coefficient r greater than 0.9990 are listed. An inspection of Table 3 shows that:

(a) For data set 1, $f(\alpha) = \alpha^{0.5}$, both m- and m, n-types of mechanism are possible, although r values for the former type are a little better than those for the latter one.

(b) For data set 2, $f(\alpha) = (1-\alpha)^{0.5}$, m-, p-, m, n- and n, p-types of mechanism are possible. The n, p-type of mechanism has the highest correlation coefficient,

Table 3

Elucidation of probable reaction mechanisms for five sets of artificial data by the extended Coats and Redfern treatment

True $f(\alpha)$	Line no.	Assumed parameters			E, kJ/mole	A, sec^{-1}	r
		m	n	p			
$\alpha^{0.5}$	1	0.0			428.73	1.115×10^{34}	0.99999
	2	0.2			341.08	5.001×10^{26}	0.99999
	3	0.4			254.14	2.463×10^{19}	0.99999
	4	0.6			170.05	2.113×10^{13}	0.99999
	5	0.8			92.48	1.052×10^{6}	0.99989
	6	0.6	0.1		193.99	2.324×10^{14}	0.99989
	7	0.8	0.1		106.93	1.118×10^{7}	0.99994
$(1-\alpha)^{0.5}$	8		0.6		215.71	1.620×10^{16}	0.99981
	9		0.4		203.86	1.299×10^{15}	0.99983
	10			−0.8	361.70	3.133×10^{28}	0.99907
	11			−1.0	407.94	2.878×10^{32}	0.99937
	12			−1.2	431.21	2.857×10^{34}	0. 99947
	13	0.5	0.5		105.00	5.416×10^{6}	0 .99980
	14	0.6	0.3		86.31	1.175×10^{5}	0.99957
	15		1/3	−1.0	434.57	7.827×10^{34}	0.99997
$[-\ln(1-\alpha)]^{-1}$	16			−1.4	258.93	9.796×10^{19}	0.99990
	17			−1.2	234.27	6.602×10^{17}	0.99997
	18			−1.0	209.83	4.652×10^{15}	1.00000
	19			−0.8	185.64	3.452×10^{13}	0.99997
	20			−0.6	161.74	2.720×10^{11}	0.99986
	21			−0.4	138.18	2.298×10^{9}	0.99963
	22			−0.2	114.99	2.110×10^{7}	0.99925
	23		0.4		102.69	2.447×10^{6}	0.99984
	24		0.2		97.23	6.811×10^{5}	0.99982
	25		1/3	−1.0	223.48	1.039×10^{17}	0.99903
$\alpha(1-\alpha)$	26	1.0	1.0		275.47	1.685×10^{22}	0.99956
$(1-\alpha)^{1/3}[-\ln(1-\alpha)]^{-1}$	27			−1.4	242.71	4.472×10^{17}	0.99954
	28			−1.2	219.49	3.930×10^{16}	0.99932
	29			−1.0	196.51	3.608×10^{14}	0.99902
	30		0.6		101.85	2.598×10^{6}	0.99994
	31		0.4		95.97	6.535×10^{5}	0.99959
	32		1/3	−1.0	209.45	7.496×10^{15}	1.00000

which is a wrong indication. If the real mechanism is of n-type, however, the unextended treatment would yield correct kinetic parameters (between lines 8 and 9).

(c) For data set 3, $f(\alpha) = [-\ln(1-\alpha)]^{-p}$, n, p- and n, p-types of mechanism are possible. The true mechanism, of course, yields the highest value of r and correct kinetic parameters.

(d) For data set 4, $f(\alpha) = \alpha(1 - \alpha)$, only the right mechanism is possible. However, the activation energy and frequency factor obtained are not correct.

(e) For data set 5, $f(\alpha) = (1 - \alpha)^{1/3} [-\ln (1 - \alpha)]^{-1}$, three types of mechanism, *n*-, *p*- and *n, p*-, are possible. The right mechanism yields the highest correlation coefficient and correct values of E and A.

It is seen, from above, that Coats and Redfern's method, even after modification, is not satisfactory to treat thermoanalytical data.

4. *Linear Least Squares Fitting (LLSF) method*

Take a common mechanism type $\alpha^m(1 - \alpha)^n$ as an example. The rate equation can be written as

$$\frac{d\alpha}{dT} = \frac{A}{\Phi} \exp(-E/RT)\alpha^m(1 - \alpha)^n. \tag{12}$$

Take logarithms:

$$\ln \frac{d\alpha}{dT} = \ln\left(\frac{A}{\Phi}\right) - \frac{E}{R}\left(\frac{1}{T}\right) + m \ln \alpha + n \ln(1 - \alpha) \tag{13}$$

Equation (13) may be written in the following form:

$$y = p_1 + p_2x + p_3z + p_4w. \tag{14}$$

The sum of square residues S is given by

$$S = \sum_{i=1}^{l} (y_i - p_1 - p_2x_i - p_3z_i - p_4w_i)^2 \tag{15}$$

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

$$\frac{\partial S}{\partial p_1} = 0, \quad \frac{\partial S}{\partial p_2} = 0, \quad \frac{\partial S}{\partial p_3} = 0 \text{ and } \frac{\partial S}{\partial p_4} = 0.$$

The normal equations may be represented by a matrix form:

$$\begin{vmatrix} \Sigma y_i \\ \Sigma x_iy_i \\ \Sigma z_iy_i \\ \Sigma w_iy_i \end{vmatrix} = \begin{vmatrix} l & \Sigma x_i & \Sigma z_i & \Sigma w_i \\ \Sigma x_i & \Sigma x_i^2 & \Sigma x_iz_i & \Sigma x_iw_i \\ \Sigma z_i & \Sigma x_iz_i & \Sigma z_i^2 & \Sigma z_iw_i \\ \Sigma w_i & \Sigma x_iw_i & \Sigma z_iw_i & \Sigma w_i^2 \end{vmatrix} \begin{vmatrix} p_1 \\ p_2 \\ p_3 \\ p_4 \end{vmatrix} \tag{16}$$

All the summations are taken from 1 to l. The four constants p_i, p_2, p_3, and p_4 can then be obtained by solving Eq. (16), and the four parameters A, E, m, and n can be calculated in turn. Similar procedures apply to the other four types of mechanism.

The five sets of artificial data were treated by the LLSF procedure. The results obtained are listed in Tables 4(a) to 4(e).

Table 4

Results from LLSF treatment for five sets of artificial data

Table 4(a)

Artificial data set 1, $f(\alpha) = \alpha^{0.5}$

Assumed $f(\alpha)$	A, sec^{-1}	E, kJ/mole	m	n	p	r
α^m	2.533×10^{20}	265.98	0.37			1.00000
$(1-\alpha)^n$	1.320×10^{34}	429.24		−0.00		1.00000
$[-\ln(1-\alpha)]^p$	1.174×10^{34}	428.82			0.00	1.00000
$\alpha^m(1-\alpha)^n$	1.802×10^{19}	252.33	0.40	0.00		1.00000
$(1-\alpha)^n[-\ln(1-\alpha)]^p$	4.674×10^{33}	423.78		0.00	0.01	1.00000

Table 4(b)

Artificial data set 2, $f(\alpha) = (1-\alpha)^{0.5}$

Assumed $f(\alpha)$	A, sec^{-1}	E, kJ/mole	m	n	p	r
α^m	#	−594.72	3.77			0.99620
$(1-\alpha)^n$	4.984×10^{15}	210.00		0.50		1.00000
$[-\ln(1-\alpha)]^p$	*	746.76			−2.42	0.99970
$\alpha^m(1-\alpha)^n$	7.340×10^{15}	211.97	0.00	0.50		1.00000
$(1-\alpha)^n[-\ln(1-\alpha)]^p$	2.011×10^{15}	205.38		0.50	0.01	1.00000

Table 4(c)

Artificial data set 3, $f(\alpha) = [-\ln(1-\alpha)]^{-1}$

Assumed $f(\alpha)$	A, sec^{-1}	E, kJ/mole	m	n	p	r
α^m	2.328×10^{-29}	−302.10	3.74			0.99894
$(1-\alpha)^n$	1.010×10^{6}	98.44		0.27		0.99988
$[-\ln(1-\alpha)]^p$	4.948×10^{15}	209.95			−1.00	1.00000
$\alpha^m(1-\alpha)^n$	1.057×10^{-3}	− 5.41	0.97	0.20		1.00000
$(1-\alpha)^n[-\ln(1-\alpha)]^p$	4.368×10^{15}	209.28		0.00	−1.00	1.00000

Table 4(d)

Artificial data set 4, $f(\alpha) = \alpha(1-\alpha)$

Assumed $f(\alpha)$	A, sec^{-1}	E, kJ/mole	m	n	p	r
α^m	#	−3562.44	2.55			0.99915
$(1-\alpha)^n$	*	2642.64		1.64		0.99965
$[-\ln(1-\alpha)]^p$	#	−9328.20			4.66	0.97341
$\alpha^m(1-\alpha)^n$	3.262×10^{15}	207.73	1.00	1.00		1.00000
$(1-\alpha)^n[-\ln(1-\alpha)]^p$	*	1585.92		1.51	0.42	0.99988

values of A are less than 10^{-41}

* values of A are greater than 10^{41}

Table 4(e)

Artificial data set 5, $f(\alpha) = (1 - \alpha)^{1/3}[-\ln(1 - \alpha)]^{-1}$

Assumed $f(\alpha)$	A, sec^{-1}	E, kJ/mole	m	n	p	r
α^m	1.308×10^{-28}	-288.28	3.65			0.99576
$(1 - \alpha)^n$	1.022×10^6	99.66		0.53		0.99997
$[-\ln(1 - \alpha)]^p$	1.930×10^{32}	398.87			-2.71	0.99991
$\alpha^m(1 - \alpha)^n$	1.696×10^4	67.83	0.30	0.49		1.00000
$(1 - \alpha)^n[-\ln(1 - \alpha)]^p$	5.654×10^{15}	210.58		0.32	-1.00	1.00000

The r values in Table 4(a) are all unity. Values of A for m- and m, n-types of mechanism are more reasonable than for the other three types. However, the value of n in the m, n-type is zero, which means that the reaction is of m-type. Agreements between the evaluated parameters and the true ones are rather poor, however.

From Table 4(b), it is seen that mechanisms of n-type, m, n-type and n, p-type are all reasonable. Their r values are also the highest. However, the value of m in the m, n-type is zero, and that of p in the n, p-type is close to zero; therefore, the mechanism is of n-type. Agreements between the evaluated parameters and the assigned ones are excellent.

Judging from the r values in Table 4(c), three types of mechanism, p-, m, n- and n, p-, are most probable for this set of data. However, the negative E value and very low frequency factor rules out the m, n-type. The zero value of n in the n, p-type leads to a p-type of mechanism. Agreements between the evaluated and assigned parameters are again excellent.

An inspection of Table 4(d) shows that only the m, n-type of mechanism is possible for data set 4. Agreements between the evaluated and assigned parameters can be considered satisfactory.

In Table 4(e), mechanism types m, n- and n, p- have the highest value of r. Since the frequency factor for the m, n-type of mechanism is not reasonable, it is concluded that the reaction follows the n, p-type of mechanism. The evaluated parameters agree well with the assigned ones.

Conclusion

From the results obtained by applying the Horowitz and Metzger, the Freeman and Carroll, the extended Coats and Redfern and the LLSF methods to five sets of artificial data for different types of mechanism, it is seen that the former two methods lead to false results for reaction mechanisms other than of n-type. The extended Coats and Redfern method can not tell the right mechanism type, except that of m, n-type. In the latter case, although the right mechanism type can be deduced, the parameters evaluated are not correct. Only the LLSF procedure can yield the right reaction mechanism and correct values of the kinetic parameters.

References

1. A. W. Coats and J. P. Redfern, Analyst, 88 (1963) 906; V. Satava, J. Thermal Anal., 5 (1973) 217.
2. J. H. Sharp and S. A. Wentworth, Anal. Chem., 41 (1969) 2060; J. Zsakó, J. Thermal Anal., 5 (1973) 239; T. Ozawa, ibid 7 (1975) 601.
3. D. T. Y. Chen, J. Thermal Anal., 6 (1974) 109; D. T. Y. Chen and P. H. Fong, ibid 8 (1975) 295; P. H. Fong and D. T. Y. Chen, ibid 8 (1975) 305.
4. B. N. N. Achar, G. W. Brindley and J. H. Sharp, Proc. Int. Clay Conf. Jerusalem 1 (1966) 67.
5. J. Sestak and G. Berggren, Thermochim. Acta, 3 (1971) 1.
6. David T. Y. Chen and Pong H. Fong, Thermochim. Acta, 18 (1977) 161.
7. J. Dankiewicz and K. Wieczorek-Ciurowa, J. Thermal Anal., 15 (1979) 11.
8. V. Šatava and F. Škvara, J. Amer. Ceram. Soc., 52 (1969) 591.
9. K. J. Nielson, Methods in Numerical Analysis, McMillan, New York, 2nd ed. (1964)
10. H. H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
11. E. S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
12. A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.