Thermochimica Acta, 107 (1986) 353–357
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

THE HEATING RATE AS A VARIABLE IN NON-ISOTHERMAL KINETICS. II. A METHOD TO EVALUATE THE NON-ISOTHERMAL KINETIC PARAMETERS USING THIS PRINCIPLE AND INTEGRATION OVER LOW RANGES OF VARIABLES

E. URBANOVICI and E. SEGAL

Chair of Physical Chemistry and Electrochemical Technology, Faculty of Chemical Engineering, Polytechnical Institute of Bucharest, Bulevardul Republicii 13, Bucharest (Romania)

(Received 10 March 1986)

In a previous note [1] a method to evaluate non-isothermal kinetic parameters using the heating rate as a variable was described. This paper deals with another method which, besides using the heating rate as variable, applies integration over small ranges of the variables.

CALCULATIONS AND RESULTS

The notation $T_i(\beta)$ will be used for a temperature corresponding to $\alpha = \alpha_i$, which depends on the heating rate β. The derivative of T_i with respect to β will generally be denoted by $\mathrm{d}T_i(\beta)/\mathrm{d}\beta$, or for a given β_l by $[\mathrm{d}T_i(\beta)/\mathrm{d}\beta]_{\beta_l}$.

Starting from the fundamental equation of non-classical non-isothermal kinetics [2]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A(v)}{\beta} \mathrm{f}(v, \alpha)\, \mathrm{e}^{-E(v)/RT} \tag{1}$$

where v represents a set of variables:

$$v = v(\alpha, T, \beta, \dots) \tag{2}$$

by integration over the closed interval $\alpha \in [\alpha_i, \alpha_k]$ one gets:

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{\mathrm{f}(v, \alpha)} = \frac{1}{\beta_{ik}} \int_{T_i(\beta)}^{T_k(\beta)} A(v)\, \mathrm{e}^{-E(v)/RT}\, \mathrm{d}T \tag{3}$$

As $T_i(\beta)$ and $T_k(\beta)$ are functions of β we shall substitute the local heating rate β_{ik} by β in eqn. (3) without altering it essentially. Thus, eqn. (3) takes the form:

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{\mathrm{f}(v, \alpha)} = \frac{1}{\beta} \int_{T_i(\beta)}^{T_k(\beta)} A(v)\, \mathrm{e}^{-E(v)/RT}\, \mathrm{d}T \tag{4}$$

0040-6031/86/$03.50

We shall consider in a first approximation that for $\alpha \in [\alpha_i, \alpha_k]$ and $\beta \in [\beta_x, \beta_y]$ the $A(v)$, $E(v)$ and $f(v, \alpha)$ can be substituted by the average values and expression: A, E and $f(\alpha)$ [2]. In such conditions eqn. (4) becomes:

$$\int_{\alpha_i}^{\alpha_k} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_i(\beta)}^{T_k(\beta)} e^{-E/RT} dT \tag{5}$$

or introducing the notation

$$\int_{\alpha_i}^{\alpha_k} \frac{d\alpha}{f(\alpha)} = Z_{ik} \tag{6}$$

one gets:

$$Z_{ik}\beta = A \int_{T_i(\beta)}^{T_k(\beta)} e^{-E/RT} dT \tag{7}$$

Taking the derivative of (7) with respect to β it turns out that:

$$Z_{ik} = A\left[e^{-E/RT_k(\beta)} \frac{dT_k(\beta)}{d\beta} - e^{-E/RT_i(\beta)} \frac{dT_i(\beta)}{d\beta}\right] \tag{8}$$

From two relationships of the form (8) with two heating rates β_x and β_y, by division one obtains:

$$\frac{e^{-E/RT_k(\beta_x)}[dT_k(\beta)/d\beta]_{\beta_x} - e^{-E/RT_i(\beta_x)}[dT_i(\beta)/d\beta]_{\beta_x}}{e^{-E/RT_k(\beta_y)}[dT_k(\beta)/d\beta]_{\beta_y} - e^{-E/RT_i(\beta_y)}[dT_i(\beta)/d\beta]_{\beta_y}} = 1 \tag{9}$$

which allows the activation energy, E, to be evaluated. In order to get $f(\alpha)$ let us consider $\alpha_j \in [\alpha_i, \alpha_k]$:

$$\alpha_j = \frac{\alpha_i + \alpha_k}{2} \tag{10}$$

In such conditions, from (8) one can write:

$$Z_{ij} = A\left[e^{-E/RT_j(\beta)} \frac{dT_j(\beta)}{d\beta} - e^{-E/RT_i(\beta)} \frac{dT_i(\beta)}{d\beta}\right] \tag{11}$$

$$Z_{jk} = A\left[e^{-E/RT_k(\beta)} \frac{dT_k(\beta)}{d\beta} - e^{-E/RT_j(\beta)} \frac{dT_j(\beta)}{d\beta}\right] \tag{12}$$

From (11) and (12) by division one gets:

$$\frac{Z_{jk}}{Z_{ij}} = \frac{e^{-E/RT_k(\beta)}\, dT_k(\beta)/d\beta - e^{-E/RT_j(\beta)}\, dT_j(\beta)/d\beta}{e^{-E/RT_j(\beta)}\, dT_j(\beta)/d\beta - e^{-E/RT_i(\beta)}\, dT_i(\beta)/d\beta} \tag{13}$$

which allows $f(\alpha)$ to be obtained.

For the two heating rates β_x and β_y, two equations of the form (13) can be written whose right-hand members will be noted by R_x and R_y. The function $f(\alpha)$ can be obtained from the equation:

$$\frac{Z_{jk}}{Z_{ij}} = R \tag{14}$$

with R given by

$$R = \frac{R_x + R_y}{2} \tag{15}$$

The pre-exponential factor can be evaluated from relationship (8)

$$A_x = \frac{Z_{ik}}{e^{-E/RT_k(\beta)}[dT_k(\beta)/d\beta]_{\beta_x} - e^{-E/RT_i(\beta)}[dT_i(\beta)/d\beta]_{\beta_x}} \tag{16}$$

A similar relationship can be written for β_y, whence:

$$\log A = \frac{\log A_x + \log A_y}{2} \tag{17}$$

APPLICATIONS

The method was checked for the non-isothermal dehydration of $CaC_2O_4 \cdot H_2O$ for three heating rates: $\beta_1 = 0.987$ K min^{-1}, $\beta_2 = 4.988$ K min^{-1} and $\beta_3 = 9.573$ K min^{-1}. The experimental data are listed in Table 1.

To get $T_i(\beta_x)$, $T_i(\beta_y)$, $[dT_i(\beta)/d\beta]_{\beta_x}$ and $[dT_i(\beta)/d\beta]_{\beta_y}$ for various α_i values, the second degree interpolation polynomial will be used: $T_i(\beta) = a_0 + a_1\beta + a_2\beta^2$.

The coefficients a_0, a_1, a_2 can be determined from the system of three equations written for each $\alpha = \alpha_i$:

$$T_i(\beta_m) = a_0 + a_1\beta_m + a_2\beta_m^2 \quad (m = 1, 2, 3)$$

TABLE 1

Experimental data for the dehydration of $CaC_2O_4 \cdot H_2O$

No.	α	T (K) $\rightarrow \beta_1 = 0.987$ K min^{-1}	T (K) $\rightarrow \beta_2 = 4.988$ K min^{-1}	T (K) $\rightarrow \beta_3 = 9.573$ K min^{-1}
1	0.10	412.2	425.3	430.8
2	0.20	418.4	434.0	441.1
3	0.30	422.8	440.2	447.6
4	0.40	426.2	445.3	453.2
5	0.50	429.2	449.2	458.0
6	0.60	431.9	453.1	462.4
7	0.70	434.0	456.8	466.2
8	0.80	436.2	460.5	470.6
9	0.90	439.0	465.1	475.6

TABLE 2

Interpolation data for $\beta_x = 2.988$ K min^{-1} and $\beta_y = 7.281$ K min^{-1}

No.	α_i	a_0 (K)	a_1 (min)	a_2 (K^{-1} min^2)	$T_i(\beta_x)$ (K)	$T_i(\beta_y)$ (K)	$(dT_i/d\beta)_{\beta_x}$ (min)	$(dT_i/d\beta)_{\beta_y}$ (min)
1	0.10	407.779	4.718	−0.242	419.72	429.30	3.272	1.194
2	0.20	413.204	5.535	−0.274	427.30	438.98	3.898	1.545
3	0.30	416.939	6.252	−0.319	432.77	445.55	4.346	1.607
4	0.40	419.739	6.897	−0.355	437.18	451.14	4.776	1.727
5	0.50	422.501	7.142	−0.359	440.64	455.47	4.997	1.914
6	0.60	424.795	7.574	−0.381	444.02	459.74	5.297	2.026
7	0.70	426.284	8.238	−0.425	447.10	463.73	5.698	2.049
8	0.80	427.986	8.767	−0.451	450.16	467.91	6.072	2.200
9	0.90	430.134	9.469	−0.493	454.03	472.94	6.523	2.290

TABLE 3

Non-isothermal kinetic parameters of dehydration of $CaC_2O_4 \cdot H_2O$

No.	α_i	α_j	α_k	E (kcal mol^{-1})	R_x	R_y	R	n	A (s^{-1})
1	0.10	0.20	0.30	27.86	1.284	1.067	1.176	1.29	1.67×10^{11}
2	0.10	0.30	0.50	24.47	1.322	1.589	1.456	1.29	3.62×10^{9}
3	0.20	0.40	0.60	23.66	1.216	1.619	1.418	1.02	1.32×10^{9}
4	0.30	0.50	0.70	23.90	1.470	1.337	1.404	0.81	1.50×10^{9}
5	0.40	0.60	0.80	22.00	1.567	1.416	1.492	0.75	1.80×10^{8}
6	0.50	0.70	0.90	22.73	1.741	2.003	1.872	0.83	4.35×10^{8}
				$\bar{E} = 24.10$				$\bar{n} = 1.00$	$\overline{\log A} = 9.33$

Once a_0, a_1 and a_2 are known, $T_i(\beta)$ and $dT_i(\beta)/d\beta$ for every $\beta \in [\beta_1, \beta_3]$ can in principle be obtained.

We shall take:

$$\beta_x = \frac{\beta_1 + \beta_2}{2} = 2.988 \text{ K min}^{-1}$$

$$\beta_y = \frac{\beta_2 + \beta_3}{2} = 7.281 \text{ K min}^{-1}$$

The interpolated data are listed in Table 2.

The non-isothermal kinetic parameters for $f(\alpha) = 1(1 - \alpha)^n$ are listed in Table 3. As seen from the table, the average values of the kinetic parameters are in satisfactory agreement with those reported in the literature [3–5].

REFERENCES

1 E. Urbanovici and E. Segal, Thermochim. Acta, 95 (1985) 273.
2 E. Urbanovici and E. Segal, Thermochim. Acta, 107 (1986) 339.
3 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
4 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
5 E. Segal, Thermochim. Acta, 53 (1982) 365.