Thermochimica Acta, 80 (1984) 389–393
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

A NEW INTEGRAL METHOD OF NON-ISOTHERMAL KINETIC DATA EVALUATION

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(Received 11 May 1984)

New formulae for calculating kinetic parameters have been derived by integration of the non-isothermal rate equation over small temperature intervals.

Following research on the integration of the non-isothermal rate equation over small temperature intervals [1], this paper deals with a new integral method for the kinetic analysis of heterogeneous reactions.

To integrate the equation

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

where in the most general case [2]

$$\mathrm{f}(\alpha)=(1-\alpha)^n\alpha^m\left[\ln\frac{1}{1-\alpha}\right]^p \tag{2}$$

and

$$A=A_rT^r \tag{3}$$

the following theorem from mathematical analysis is used [3]: if the functions f(x) and g(x) are continuous in the closed interval $[a, b]$, and g(x) does not change its sign in this interval, there is a point, $\xi \in (a, b)$, such that

$$\int_a^b \mathrm{f}(x)\mathrm{g}(x)\mathrm{d}x=\mathrm{f}(\xi)\int_a^b \mathrm{g}(x)\mathrm{d}x \tag{4}$$

Taking into account relationship (3), through separation of the variables in eqn. (1) one gets

$$\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)}=\frac{A_r}{\beta}T^r\,\mathrm{e}^{-E/RT}\mathrm{d}T \tag{5}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)}=\frac{A_r}{\beta}T^{r+2}\frac{\mathrm{e}^{-E/RT}}{T^2}\mathrm{d}T \tag{6}$$

Equation (6) is integrated between the limits $(\alpha_i, \alpha_j) \rightarrow (T_i, T_j)$ with the conditions $T_j > T_i$ and $T_j - T_i \leq 15$. The difference $\alpha_j - \alpha_i$ should be sufficient not to be sensitive to errors in measuring α values. Taking into account relationship (4) the integration of eqn. (6) leads to

$$\int_{\alpha_i}^{\alpha_j} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \frac{A_r}{\beta} T_{ij}^{r+2} \int_{T_i}^{T_j} \frac{\mathrm{e}^{-E/RT}}{T^2} \mathrm{d}T \tag{7}$$

Taking T_{ij} as

$$T_{ij} = \frac{T_i + T_j}{2} \tag{8}$$

and introducing the notation

$$\int_{\alpha_i}^{\alpha_j} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \mathrm{F}(ij) \tag{9}$$

eqn. (7) becomes

$$\mathrm{F}(ij) = \frac{A_r}{\beta} T_{ij}^{r+2} \frac{R}{E} (\mathrm{e}^{-E/RT_j} - \mathrm{e}^{-E/RT_i}) \tag{10}$$

Choosing the temperatures T_1, T_2 and T_3 so that $T_1 < T_2 < T_3$, and

$$T_3 - T_2 = T_2 - T_1 = \Delta T \tag{11}$$

and taking into account eqn. (10), the following two equations can be written

$$\mathrm{F}(1, 2) = \frac{A_r}{\beta} \frac{R}{E} T_{12}^{r+2} (\mathrm{e}^{-E/RT_2} - \mathrm{e}^{-E/RT_1}) \tag{12}$$

$$\mathrm{F}(2, 3) = \frac{A_r}{\beta} \frac{R}{E} T_{23}^{r+2} (\mathrm{e}^{-E/RT_3} - \mathrm{e}^{-E/RT_2}) \tag{13}$$

From eqns. (12) and (13) one gets

$$\frac{\mathrm{F}(2, 3)}{\mathrm{F}(1,2)} \left(\frac{T_{12}}{T_{23}} \right)^{r+2} = \frac{\mathrm{e}^{-E/RT_3} - e^{-E/RT_2}}{\mathrm{e}^{-E/RT_2} - e^{-E/RT_1}} \tag{14}$$

or

$$\mathrm{G} = \frac{\mathrm{e}^{E\Delta T/RT_2T_3} - 1}{1 - \mathrm{e}^{-E\Delta T/RT_1T_2}} \tag{15}$$

where

$$\mathrm{G} = \frac{\mathrm{F}(2, 3)}{\mathrm{F}(1, 2)} \left(\frac{T_{12}}{T_{23}} \right)^{r+2} \tag{16}$$

Introducing the notation

$$a = \frac{\Delta T}{RT_1T_2} \qquad b = \frac{\Delta T}{RT_2T_3} \tag{17}$$

and taking into account the developments

$$e^{x} = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots \qquad e^{-x} = 1 - \frac{x}{1!} + \frac{x^2}{2!} - \frac{x^3}{3!} + \ldots \tag{18}$$

we shall work on relationship (16).

(1) Considering the first three terms in eqn. (18) one gets

$$G = \frac{1 + Eb + \dfrac{E^2b^2}{2} - 1}{1 - 1 + Ea - \dfrac{E^2a^2}{2}} \tag{19}$$

whose solution with respect to E is:

$$E = \frac{2RT_2T_3}{\Delta T}\,\frac{T_3/T_1G - 1}{(T_3/T_1)^2G + 1} \tag{20}$$

If, for a given f(α) and r, the E values calculated by eqn. (20) for different temperature sets are close to each other, then f(α) and r have been correctly chosen. The necessary temperature sets are indicated in the following scheme

$$\begin{array}{ccccccc} & & \text{II} & & \text{IV} & & \\ T_1 & T_2 & T_3 & T_4 & T_5 & T_6 & T_7 \\ & \text{I} & & \text{III} & & \text{V} & \end{array}$$

(2) Taking four terms from eqn. (18)

$$G = \frac{1 + Eb + \dfrac{E^2b^2}{2} + \dfrac{E^3b^3}{6} - 1}{1 - 1 + Ea - \dfrac{E^2a^2}{2} + \dfrac{E^3a^3}{6}} \tag{21}$$

which, through simple calculations, becomes

$$E^2(a^3G - b^3) - 3E(a^2G + b^2) + 6(aG - b) = 0 \tag{22}$$

which can be solved with respect to E. Obviously, for different temperature sets, if f(α) and r are correctly chosen, the same values for the activation energy should be obtained. In practical calculations eqn. (20) is used for simplicity. Once the activation energy is known, the pre-exponential factor, A_r, can be obtained from eqn. (10)

$$A_r = \frac{E\beta \mathrm{F}(ij)}{T_{ij}^{r+2} R\left(\mathrm{e}^{-E/RT_j} - \mathrm{e}^{-E/RT_i}\right)} \tag{23}$$

To check the validity is this method it was applied to the dehydration of calcium oxalate monohydrate

$$\mathrm{CaC_2O_4 \cdot H_2O(s) \rightarrow CaC_2O_4(s) + H_2O(g)} \tag{I}$$

with $r = 0$; $\Delta T = 15$ K; $\beta = 10$ K min^{-1}. The results are given in the following table.

No.	Temperature set (K)	E (kcal mol^{-1}), $n = 0.9$	E (kcal mol^{-1}), $n = 1$
1	473, 488, 503	25.02	25.62
2	488, 503, 518	22.04	23.38
3	503, 518, 533	22.52	25.51
4	478, 493, 508	17.76	18.54
5	493, 508, 523	25.62	27.27
6	483, 498, 513	22.09	23.24
7	498, 513, 528	21.15	23.32

To evaluate which of the two sets of activation energy values best describes the chosen test reaction, the mean values, $\bar{x}$, and the dispersions, s, have been calculated [4], according to the formulae

$$x = \frac{1}{q} \sum x_i \tag{24}$$

where $x_i (i = 1, 2, \ldots q)$ are individual values, and

$$s = \sqrt{\left[\frac{1}{q-1} \sum_{i=1}^{q} (x_i - \bar{x})^2\right]} \tag{25}$$

The results are: $n = 1$, $E = 23.84$ kcal mol^{-1}, s $= 2.79$; $n = 0.9$, $E = 22.32$ kcal mol^{-1}, $s = 2.60$.

Since the dispersion is lower for $n = 0.9$, it turns out that for the dehydration of calcium oxalate monohydrate, $\mathrm{f}(\alpha) = (1 - \alpha)^{0.9}$. Using the value $E = 22.32$ kcal mol^{-1}, and relationship (23), we obtained the mean value of the pre-exponential factor, $\bar{A}$ (the individual values were obtained for different values of the temperatures T_i and T_j)

$$\bar{A} = 2.1 \times 10^7 \text{ s}^{-1}$$

Thus, the proposed integral method led to

$$n = 0.9, E = 22.32 \text{ kcal mol}^{-1}; A = 2.1 \times 10^7 \text{ s}^{-1}$$

which are in fairly good agreement with the literature [5–7].

CONCLUSIONS

A new integral method to evaluate non-isothermal kinetic parameters was proposed. The kinetic parameter values for the dehydration of calcium oxalate monohydrate obtained with this method are in good agreement with those reported in the literature.

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