Thermochimica Acta, 70 (1983) 359–362
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

ON THE TEMPERATURE RANGE OF THE DECOMPOSITION IN NON-ISOTHERMAL KINETICS

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(Received 10 March 1983)

The aim of the present work is to determine the dependence of the decomposition temperature range on the kinetic parameters.

In order to perform the necessary calculation the following assumptions have been made:

(a) the rate equation of a heterogeneous reaction is

$$\mathrm{d}\alpha/\mathrm{d}t = \mathrm{f}(\alpha)\mathrm{g}(T) \tag{1}$$

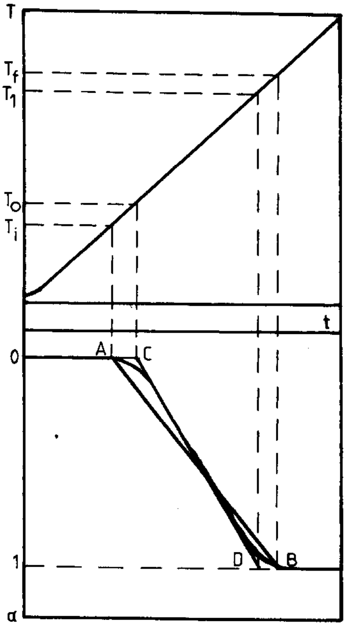

Fig. 1. Straight lines approximating the $\alpha(t)$ curves.

(b) $g(T)$ follows the Arrhenius equation

$$g(T) = A \exp(-E/RT) \tag{2}$$

(c) $f(\alpha)$ is given as

$$f(\alpha) = (1-\alpha)^n \tag{3}$$

where n is the reaction order;

(d) heating rate, $\beta = dT/dt$, is constant;

(e) the curve $\alpha(T)$ can be approximated by a straight line.

The last assumption requires more explanation. As shown in Fig. 1, when α changes from 0 to 1, the temperature changes from T_i to T_f. The AB straight line can be considered as a first approximation of $\alpha(T)$, but it is seen to be too rough. A better approximation seems to be the CD line, which has to be drawn as near as possible to almost all $\alpha(T)$ points. It provides two different temperatures, T_0 and T_1, which can be considered as the true initial and final temperatures. Their difference, ΔT, is the temperature range within which the reaction occurs.

Taking these assumptions into account

$$\alpha = \frac{T - T_0}{\Delta T} \tag{4}$$

$$\frac{d\alpha}{dT} = \frac{1}{\Delta T} \tag{4a}$$

$$1 - \alpha = \frac{T_1 - T}{\Delta T} \tag{4b}$$

Equation (1) with eqns. (2), (3) and (4b) becomes

$$\frac{d\alpha}{dT} = A\frac{1}{\beta}\frac{1}{(\Delta T)^n}(T_1 - T)^n \exp(-E/RT) \tag{5}$$

where A is the pre-exponential factor, E is the activation energy, and $R = 1.987$ cal K^{-1}.

Equation (5) can be integrated for α from 0 to 1 and temperature from T_0 to T_1 to give

$$1 = \frac{A}{\beta(\Delta T)^n}\int_{T_0}^{T_1}(T_1 - T)^n \exp(-E/RT)\, dT \tag{6}$$

The integral can be solved using the same methods as those for the temperature integral [1–3]. The solution is, then, approximated as

$$\int_{T_0}^{T_1}(T_1 - T)^n \exp(-E/RT)\, dT = \frac{R}{E}(\Delta T)^{n+2} \exp(-E/RT_0) \tag{7}$$

Equations (6) and (7) lead to

$$\Delta T = \sqrt{\beta\frac{E}{AR}\exp(E/RT_0)} \tag{8}$$

Equation (8) gives the dependence of the decomposition temperature range on the kinetic parameters. It seems to show that the reaction order hypothesis does not influence the range within which the reaction occurs.

Equation (8) can be used for different heating rates to obtain the activation energy and pre-exponential factor

$$\left(\frac{\Delta T_i}{\Delta T_j}\right)^2=\frac{\beta_i}{\beta_j}\exp\left(\frac{E}{R}\frac{T_{0j}-T_{0i}}{T_{0i}T_{0j}}\right) \tag{9}$$

where β_i and β_j are two different heating rates, $\beta_j>\beta_i$, and ΔT_i, ΔT_j, T_{0i}, and T_{0j} are the corresponding temperature differences and temperatures, respectively.

From eqn. (9)

$$E=R\frac{T_{0i}T_{0j}}{T_{0j}-T_{0i}}\ln\left(\frac{\Delta T_i}{\Delta T_j}\right)^2\frac{\beta_j}{\beta_i} \tag{9a}$$

Using the data for the dehydration of calcium oxalate given in ref. 4, $E=23\,445$ cal mole^{-1} and $A=10^{12}$ s^{-1} are obtained as medium values. With the same assumptions (a, b, c, d and e) and taking into account the maximum values of the decomposition rate, a relation for the reaction order, n, can be derived. When $\mathrm{d}^2\alpha/\mathrm{d}t^2=0$, it follows that

$$n\left.\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right|_{\mathrm{m}}=\frac{E}{RT_{\mathrm{m}}^2}(1-\alpha_{\mathrm{m}}) \tag{10}$$

where "m" refers to the value measured for the maximum decomposition rate. Taking into account eqns. (4a) and (4b) and re-arranging the terms

$$n=\frac{E}{R}\left(\frac{T_1-T_{\mathrm{m}}}{T_{\mathrm{m}}^2}\right) \tag{11}$$

Using the same data as before [4] and the E value determined according to eqn. (8), $n=0.7$ is obtained.

CONCLUSION

An equation of the temperature range dependence on the kinetic parameters [eqn. (8)] based on some simplified assumptions is given. The equation has been used to determine the kinetic parameters. The values obtained, for calcium oxalate dehydration, $E=23\,445$ cal mole^{-1}, $A=10^{12}$ s^{-1} and $n=0.7$, are close to those published previously [5,6]. Probably $n=1$ is the correct value for the considered reaction. This is supported by the value of the pre-exponential factor, which is in close agreement with that predicted by Transition State Theory [6].

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