Thermochimica Acta, 57 (1982) 247–250
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

Note

THE SHAPE OF THE THERMOANALYTICAL CURVES AT HYPERBOLIC TEMPERATURE PROGRAMS

GABOR VÁRHEGYI

Hungarian Academy of Sciences, Research Laboratory for Inorganic Chemistry, Budapest (Hungary)

(Received 19 February 1982)

For the sake of the simplicity of the mathematical deductions, several researchers have proposed the use of hyperbolic temperature programs in non-isothermal reaction kinetics [1–3]. For hyperbolic temperature programs, the reciprocal of the temperature is a linear function of time

$$1/T = u - vt \tag{1}$$

where u and v are constant parameters.

Since the differentiation of eqn. (1) gives $\mathrm{d}t = -v^{-1}\mathrm{d}(1/T)$, the integration of $\mathrm{e}^{-E/RT}$ by t can be carried out analytically

$$\int \mathrm{e}^{-E/RT}\,\mathrm{d}t = -\frac{1}{v}\int \mathrm{e}^{-E/RT}\,\mathrm{d}\frac{1}{T} = \frac{R}{vE}\,\mathrm{e}^{-E/RT} \tag{2}$$

Let x be the reacted mole fraction, and $\mathrm{f}(x)$ be a function with positive values in the interval (0, 1). If eqn. (1) is valid and the kinetic equation of the studied process has the form

$$\mathrm{d}x/\mathrm{d}t = A\,\mathrm{e}^{-E/RT}\mathrm{f}(x) \tag{3}$$

then, by simple integration [1]

$$\mathrm{g}(x) = \frac{AR}{vE}\,\mathrm{e}^{-E/RT} \tag{4}$$

Here $\mathrm{g}(x)$ is the integral of $1/\mathrm{f}(x)$. Equation (4) is considerably simpler than the corresponding equations of the linear temperature programs and in this way evaluation of the unknown kinetic parameters is also simpler. Although it is doubtful whether the mathematical simplicity is well worth developing sophisticated instruments, the study of the fundamental properties of the thermoanalytical curves for non-linear temperature programs has some theoretical interest.

In the present paper, the shape of the thermoanalytical curves is examined. Following the conception of Horowitz and Metzger [4], the shape of

0040-6031/82/0000–0000/$02.75

the curve is characterized by the reacted mole fraction at the peak maximum (for symmetrical curves this quantity is 0.5). The present paper aims to:

(i) provide simple mathematical examples for the study of the effects of non-linearity of temperature programs [5]; and

(ii) give information for the kinetic evaluation of measurements for hyperbolic heating programs.

THE SHAPE OF CURVES $x(t)$

In this section, the reacted mole fraction, x, is regarded as a function of time, and the value of x at which dx/dt is maximal is determined. By the combination of eqns. (3) and (4), dx/dt can easily be expressed as a function of x

$$dx/dt = v\frac{E}{R}f(x)g(x) \tag{5}$$

The condition of the peak maximum of curve $(dx/dt)(t)$ is $d^2x/dt^2 = 0$. Differentiating eqn. (5) and dividing it by the factors common in the arising terms gives

$$f(x)\, dg/dx + g(x)\, df/dx = 0 \tag{6}$$

Since $g(x)$ is the integral of $1/f(x)$, the first term is equal to 1 and

$$-g(x)\, df/dx = 1 \tag{7}$$

A similar equation can also be obtained for linear heating programs [6], but in that case the value of the right-hand side depends on E and A. Substituting actual $f(x)$ functions into eqn. (7), relationships can be obtained between the unknown parameters of $f(x)$ and the reacted mole fraction of the peak maximum. If $f(x) = (1-x)^n$ and $n > 0$, the solution of eqn. (7) gives Gorbachev's equation [3] for the reacted mole fraction at the peak maximum

$$\begin{aligned} x &= 1 - n^{1/(1-n)} \qquad n \neq 1 \\ x &= 1 - e^{-1} \qquad n = 1 \end{aligned} \tag{8}$$

Equation (8) was originally deduced by Horowitz and Metzger [4] for linear heating rates. However, it can be shown that at high values of n eqn. (8) is a poor approximation of the correct equation for the linear heating programs. At $n = 2$, for example, the application of eqn. (8) at a linear $T(t)$ results in an error of $\Delta n \cong -0.25$, while at $n = 3$ the error would be about -0.5 [5]. (Since n is usually only a formal reaction order in solid state reactions, we cannot exclude the possibility of values of n higher than 2.)

THE SHAPE OF CURVES $x(T)$

In this section, the reacted mole fraction, x, is regarded as a function of temperature, and the value of x at which the slope of curve $x(T)$ is maximal is determined. Since $\mathrm{d}x/\mathrm{d}T = (\mathrm{d}x/\mathrm{d}t)\,(\mathrm{d}t/\mathrm{d}T)$ and eqn. (1) gives $\mathrm{d}t/\mathrm{d}T = v^{-1}\,T^{-2}$, eqn. (5) should be transformed into

$$\mathrm{d}x/\mathrm{d}T = \frac{E}{R}\mathrm{f}(x)\mathrm{g}(x)T^{-2} \tag{9}$$

The condition of the maximum of $\mathrm{d}x/\mathrm{d}T$ is $\mathrm{d}^2x/\mathrm{d}T^2 = 0$. Differentiating eqn. (8) by T and dividing it by $(E/R)\,(\mathrm{d}x/\mathrm{d}T)T^{-2}$ gives

$$\mathrm{f}(x)\,\mathrm{dg}/\mathrm{d}x + \mathrm{g}(x)\,\mathrm{df}/\mathrm{d}x - 2\mathrm{f}(x)\mathrm{g}(x)T^{-1}(\mathrm{d}x/\mathrm{d}T)^{-1} = 0 \tag{10}$$

Substituting eqn. (8) for $\mathrm{d}x/\mathrm{d}t$ and considering that $\mathrm{dg}/\mathrm{d}x$ is equal to $1/\mathrm{f}(x)$, gives

$$-\mathrm{g}(x)\,\mathrm{df}/\mathrm{d}x = 1 - 2RT/E \tag{11}$$

Since E/RT is usually between 20 and 50, the right-hand side is between 0.9 and 0.96.

In the case of linear temperature programs, the following equation can be deduced [6]

$$-\mathrm{g}(x)\,\mathrm{df}/\mathrm{d}x = q(E/RT) \tag{12}$$

where $q(E/RT)$ is the function arising from the integral of $\mathrm{e}^{-E/RT}$ by T

$$\int_0^T \mathrm{e}^{-E/RT}\,\mathrm{d}T = RT^2E^{-1}q(e/RT)\,\mathrm{e}^{-E/RT} \tag{13}$$

If eqn. (13) is regarded as the definition of the function $q(E/RT)$, then eqn. (13) is exact. If a finite series or a Padé approximation is substituted in the place of q, then eqn. (13) is obviously an approximation. Equations analogous to eqn. (13) are widely used in the literature of thermal analysis. The simplest of the available approximations of q is

$$q(E/RT) \cong 1 - 2RT/E \tag{14}$$

This approximation can be found, among others, in the works of Kissinger [7] and Coats and Redfern [8]. A comparison of eqns. (11), (12) and (14) shows that the reacted mole fraction belonging to the maximum of $\mathrm{d}x/\mathrm{d}T$ is approximately the same for hyperbolic and linear temperature programs while, as shown in the previous section, the reacted mole fraction belonging to the maximum of $\mathrm{d}x/\mathrm{d}t$ may be significantly different for hyperbolic and linear $T(t)$.

ACKNOWLEDGEMENTS

The author thanks Professor Gy. Varsányi for his valuable advice.

REFERENCES

1 J. Zsako, J. Therm. Anal., 2 (1970) 459.
2 J. Simon, J. Therm. Anal., 3 (1971) 301.
3 V.M. Gorbachev, J. Therm. Anal., 10 (1976) 191.
4 H.H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
5 G. Várhegyi, Thermochim. Acta, in press.
6 G. Várhegyi and T. Székely, Thermochim. Acta, 57 (1982) 13.
7 H.E Kissinger, Anal. Chem., 29 (1957) 1702.
8 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.