

Short Communications

THE PEAK OF THE DERIVATIVE THERMOANALYTICAL CURVE OF DIFFUSION

T. OZAWA

Electrotechnical Laboratory, Tanashi, Tokyo, Japan

(Received October 3, 1972)

The conversion, the reduced rate of conversion $dC/d\Theta$ and Θ at the peak of derivative thermoanalytical curve of diffusion are estimated theoretically, solving the theoretical equation with an electronic digital computer. These values for chemical reactions including random degradation of polymers are also estimated and compared with those of diffusion. The conversion at the peak is utilized to elucidate preliminarily the mechanism of the process.

In a previous paper [1], the author dealt with non-isothermal kinetics of diffusion and its application to the kinetic analysis of thermoanalytical curves. It was elucidated that the conversion, C , is a single-valued function of the reduced time, ϑ , such that in the case of a chemical reaction [2]:

$$C = \Phi(\vartheta) \quad (1)$$

where ϑ equals $\int_0^t h(T)dt$, and t , T and $h(T)$ are the time, the temperature and the function of the temperature-dependence of the diffusion constant, D , respectively; i.e. D equals $D_0 h(T)$, and D_0 is a constant. When the temperature-dependence of D is of the Arrhenius type:

$$D = D_0 \exp(-\Delta E/RT) \quad (2)$$

ϑ equals $\Delta EP(\Delta E/RT)/\alpha R$, where ΔE , R , α and $P(x)$ are the activation energy, the gas constant, the heating rate and the p -function [3], respectively.

As elucidated previously [1], we have the following equation for the peak of the derivative thermoanalytical curve obtained at constant heating rate:

$$\left(\frac{dC}{d\vartheta}\right)_m + \left(\frac{d^2C}{d\vartheta^2}\right)_m \vartheta_m = 0 \quad (3)$$

where the subscript m denotes the peak, and $p(x)$ is approximated to be $\exp(-x)/x^2$ [3], since the second derivative of the conversion d^2C/dt^2 equals zero at the peak.

In the previous paper [1], Θ is defined as follows

$$\Theta = \frac{1}{a^2} \int_0^t D dt \quad (4)$$

where a is the radius for a sample of spherical or cylindrical shape, or the thickness for an infinite plate. When the temperature-dependence of D is of the Arrhenius type, Θ is equal to $D_0 \Delta EP (\Delta E/RT)/\alpha a^2 R$ in the case of constant heating rate. Thus, we obtain

$$\left(\frac{dC}{d\Theta}\right)_m + \left(\frac{d^2C}{d\Theta^2}\right)_m \Theta_m = 0 \quad (5)$$

Now Eq. (5) can be solved, because $dC/d\Theta$ and $d^2C/d\Theta^2$ are both functions of Θ : for the spherical sample

$$\frac{dC}{d\Theta} = 6 \sum_{n=1}^{\infty} \exp(-n^2 \pi^2 \Theta) \quad (6)$$

$$\frac{d^2C}{d\Theta^2} = -6\pi^2 \sum_{n=1}^{\infty} n^2 \exp(-n^2 \pi^2 \Theta) \quad (7)$$

for the cylindrical sample

$$\frac{dC}{d\Theta} = 4 \sum_{n=1}^{\infty} \exp(-\beta_n^2 \Theta) \quad (8)$$

$$\frac{d^2C}{d\Theta^2} = -4 \sum_{n=1}^{\infty} \beta_n^2 \exp(-\beta_n^2 \Theta) \quad (9)$$

where the β_n 's are the roots of the Bessel function of the zero-th order, and for the plate-like sample

$$\frac{dC}{d\Theta} = 8 \sum_{n=0}^{\infty} \exp\{-(2n+1)^2 \pi^2 \Theta\} \quad (10)$$

$$\frac{d^2C}{d\Theta^2} = -8\pi^2 \sum_{n=0}^{\infty} (2n+1)^2 \exp\{-(2n+1)^2 \pi^2 \Theta\} \quad (11)$$

Applying Newton's method, we can solve these equations with an electronic digital computer, and we can further estimate the conversion and $dC/d\Theta$ at the peak by using the relations of these value with Θ [1]. The values obtained are listed in Table 1, together with those for the chemical reactions, for purposes of comparison.

The conversions at the peak for diffusion are different from those for the chemical reactions. This fact may be utilized to elucidate preliminarily the mechanism of the process. It is interesting to note that the conversions at the peak for diffusion are almost the same for the different shapes of the sample, though the Θ 's are different, and that all the conversions at the peak for diffusion are between that for the first order reaction and that for the 0.5th order reaction. It is apparent from the values of Θ_m that the derivative thermoanalytical curve for diffusion

Table 1

The conversion, $dC/d\Theta$ and Θ at the peak of derivative thermoanalytical curve

Mechanism	Conversion	$dC/d\Theta^*$	Θ^*
Diffusion (spherical sample)	0.716	2.99	0.796
Diffusion (cylindrical sample)	0.725	1.62	0.160
Diffusion (plate-like sample)	0.701	2.95	0.101
0th order reaction	1	1	1
0.5th order reaction	0.750	0.5	1
1st order reaction	0.632	0.368	1
1.5th order reaction	0.556	0.296	1
2nd order reaction	0.5	0.25	1
3rd order reaction	0.423	0.192	1
Random degradation $L = 2$	0.584	0.764	0.859
Random degradation $L = 3$	0.590	0.560	1.482
Random degradation $L = 4$	0.592	0.440	1.723
Random degradation $L = 5$	0.593	0.361	1.855
Random degradation $L = 6$	0.593	0.306	1.938

* For the chemical reactions, Θ is equal to $A \int_0^t \exp(-\Delta E/RT) dt$, namely $A\theta$, where A is the pre-exponential factor.

of the spherical sample reaches the peak at the lowest temperature, while that of the cylindrical sample does so at the highest temperature, if a and the other experimental conditions are the same for these three shapes of the sample.

References

1. T. OZAWA, *J. Thermal Anal.*, 5 (1973) 563.
2. T. OZAWA, *ibid.*, 2 (1970) 301.
3. C. D. DOYLE, *Nature*, 207 (1965) 290; *J. Appl. Polymer Sci.*, 6 (1962) 639.