Thermochimica Acta, 92 (1985) 89-92
Elsevier Science Publishers B.V., Amsterdam

THE APPLICATION OF EMPIRICAL QUANTITIES DESCRIBING THE SHAPE OF THERMOANALYTICAL CURVES

György Pokol, Sándor Gál and Ernő Pungor
Institute for General and Analytical Chemistry
Technical University of Budapest
Budapest 1521 HUNGARY

ABSTRACT

Empirical parameters - related to peak position, width, sharpness and asymmetry - were used to describe the shape of thermoanalytical curves. The reproducibility of these parameters is shown on the example of $Al/OH/_3$ DSC curves. A method is suggested for the estimation of kinetic parameters.

INTRODUCTION

Identification of materials and estimation of physico-chemical parameters requires a comparison of thermoanalytical curves. In the former case the differences between the shape of experimental curves are evaluated, in the latter, the theoretical curve most similar to the measured one is searched. The curves may be compared by fitting /with a least squares procedure/ or by means of quantities describing the shape of the curve. Such quantities /e.g. the shape index of DTA peaks/ have been used in kinetic calculations for a long time [1-4]. The present authors tested a number of empirical quantities /properties/ in the evaluation of DSC peaks of $Al/OH/_3$ dehydration [5] and simulated curves [6].

The simulated curves, in addition to a peak described by the common kinetic equation

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot (1-\alpha)^n \qquad /1/$$

contained noise and baseline components as well. Considering the experimental reproducibility of the properties, their sensitivity to the changes of kinetic parameters and to the distorting effects of noise and baseline, several properties were selected for further applications:

a. the temperature of the maximum T(Max) and the first relative

---

Proceedings of ICTA 85, Bratislava

Table 1. Averages and standard deviations from gibbsite DSC runs

	T(Max) K	M_{1R} K	W K	$\Delta T(0.8,0.2)$ K	U	α(Max)	R(0.6)	R(Max)
Average	576	567.3	34.9	26.2	0.75	0.675	0.729	0.80
S.D.	1	0.4	0.6	0.4	0.01	0.010	0.003	0.02
R.S.D.%			2	1.5	1		0.4	1.5

moment M_{1R} i.e. the center of gravity of the peak characteristic of the position of the peak along the T axis; b. the reciprocal of the maximum rate $W=d\alpha/dT^{-1}_{Max}$ and the difference between temperatures belonging to 80 and 20% conversion $\Delta T(0.8,0.2)$ connected to peak width; c. the ratio $U=\Delta T(0.8,0.2)/W$ characterizing the sharpness of the peak; d. the conversion at the maximum $\alpha(Max)$ and ratios $R(0.6)= =\Delta T(0.6,0.2)/\Delta T(0.8,0.2)$ and $R(Max)=[T(Max)-T(\alpha=0.2)]/\Delta T(0.8,0.2)$ related to asymmetry. From the aspect of the information concent of thermoanalytical curves, the position, width and asymmetry will be discussed by Várhegyi [7].

The data in Table 1 - obtained from seven replicate DSC peaks of the gibbsite $\rightarrow\chi$-alumina reaction - show good reproducibility of empirical parameters.

A METHOD TO ESTIMATE KINETIC PARAMETERS

Simulations in the present studies were based on eqn.1 and covered the ranges $9.10^3 \leq E/R \leq 2.5.10^4$ K, $10^8 \leq A \leq 10^{14}$ s^{-1} and $1/10 \leq n \leq 4/3$. Computations were carried out with the procedure described previously [5,6]. The results show that the parameters characterizing the location and width are practically linear functions of the activation energy provided A and n are fixed. If A is changed and the other two parameters are constant, the same properties gave moderately curved plots. Changing the formal order leaves T(Max) and M_{1R} almost unaffected while it has a marked influence on he width.

The properties related to the sharpness and asymmetry of the peak were found independent from E and A. As functions of the formal order, they are plotted in Fig.1. Using the data of Table 1, n=2/3 corresponding to a 3D contracting envelope applies to the DSC peaks of gippsite dehydration, with an uncertainty less than 0.1.

For a simplified treatment let us assume that an accurate n is obtained first. Then the preexperimential coefficient and the acti-

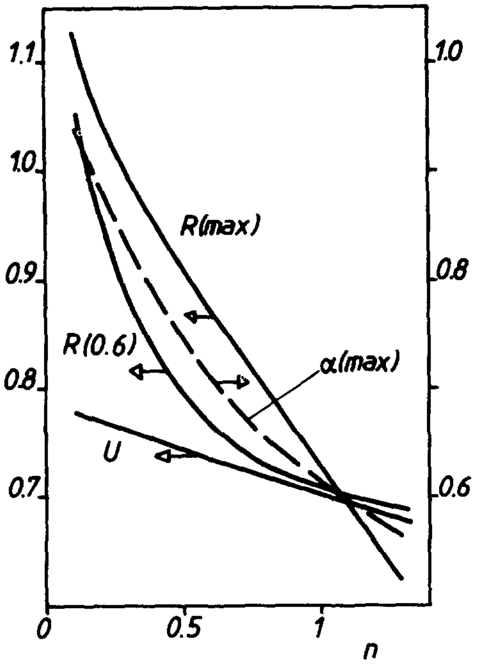

Figure 1. Parameters depending on the formal order

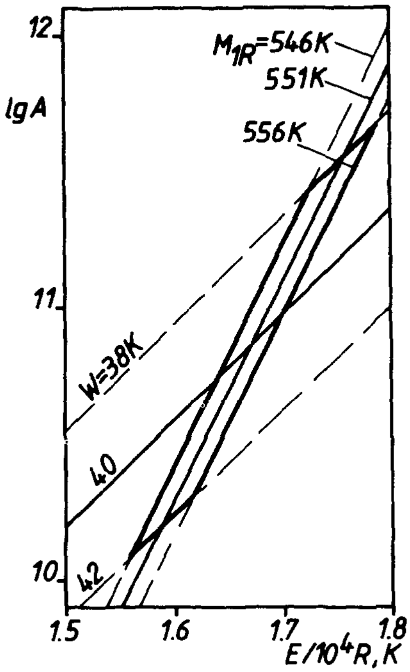

Figure 2. The estimation of E and A ; n=2/3

vation energy should be estimated on the basis of properties related to peak position and width. This problem can be solved in a logA - E/R diagram as shown in Fig.2 for n=2/3. Let us assume that we are evaluating a peak having a center of gravity M_{1R}=551 K and width W=40 K. From a set of curves simulated with n=2/3 whose A and E values form a grid in the range of interest, practically linear lines of M_{1R} and W levels can be determined. The intersection of the M_{1R}=551 K and W=40 K lines will yield the solution. /In the same way, $A=6.1\times10^{13} s^{-1}$ and E=170 kJ/mol is obtained from the values in Table 1./

Of course, M_{1R} and W may have an error. Thus, a region of solutions is defined by the intersection of the confidence intervals of the properties used [8]. In Fig.2, such a region corresponding to M_{1R}=551±5 K and W=40±2K is bordered by thick lines. /Experimental reproducibilities are frequently better than these values./ The area of solutions is extended; the difference between the highest and lowest E in the region is about 16 kJ/mol. In other words:

the estimated activation energy and preexponential factor are not independent, reflecting the well known nature of eqn.1.

Generally, the formal order is also uncertain. Consequently, using the method of intersecting zones will yield a 3D region in the lgA - E/R - n space, and the error of n will contribute to those of A and E. In the example shown in Fig.2 a ± 0.1 uncertainty of the formal order will increase the error limit of E to ± 15 kJ/mol.

DISCUSSION

If eqn.1 is valid, the preexponential factor, the activation energy and the formal order can be estimated from the quantities characterizing the shape of thermoanalytical curves. The procedure described here requires at least three empirical parameters related to peak position, width and sharpness or asymmetry. Using more than three quantities in the estimation may be useful when there is a doubt about the validity of eqn.1. /E.g. the n values obtained from different properties should agree./

The efficiency of the suggested calculation method has been compared to that of least squares model fitting; the results of that study are to be published elsewhere.

REFERENCES

1 H.E.Kissinger, Anal.Chem., 29 /1957/ 1702
2 E.Koch: Non-isothermal reaction analysis, Academic Press, London 1977
3 M.Balarin, Thermochim.Acta, 33 /1979/ 341
4 G.Várhegyi and T.Székely, Thermochim.Acta, 57 /1982/ 13
5 Gy.Pokol and S.Gál, Anal.Chim.Acta, in press
6 Gy.Pokol, S.Gál and E.Pungor, Anal.Chim.Acta, in press
7 G.Várhegyi, 8th Int.Conf.Thermal Analysis
8 L.Jánossy: Theory and practice of the evaluation of measurements, Clarendon Press, Oxford 1965