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ON THE KINETIC ANALYSIS OF DTA CURVES

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ABSTRACT

It is shown that methods of kinetic analysis, which have been developed for DTG, are not directly applicable to DTA. This is because the reaction rate, $-dx/dt$, is not proportional to the DTA signal ΔT, but rather to $\Delta T + (C/K)d(\Delta T)/dt$, where C is the heat capacity of the sample and K is the heat transfer coefficient. Only when the sample is small, the error arising from using these methods for DTA is negligible. This is demonstrated for 'computer DTA curves'. A method for the kinetic analysis of general DTA peaks is suggested.

INTRODUCTION

The applicability of methods, which were developed for kinetic analysis of DTG, to DTA curves, was discussed by several authors [e.g. 1-6]. The purpose of this paper is to examine the problem quantitatively, and to estimate the error which is involved in the results, when DTA peaks are analysed by such methods.

THEORY

The reaction rate of many reactions, which are studied by thermal methods, can be described by the equation

$$-dx/dt = Z\ f(x)\ \exp(-E/RT)\ , \qquad (1)$$

where x is the fraction of the sample not yet reacted (x is 1 at the beginning of the reaction, and 0 at its end), E is the activation energy, R is the ideal gas constant, T is the absolute temperature and Z is called the pre-exponential factor; f(x) is a simple function of x, such as x^b, where $1 \le b \le 2$.

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In the DTG method, -dx/dt is recorded versus T while the sample is heated at a linear heating rate. Many methods have been suggested for evaluating the kinetic parameters E and Z for a given DTG curve [3].

In the DTA method, the signal which is recorded as a function of time is the difference between the temperature of the sample (T_s) and that of a reference material (T_r), when both are heated up in a furnace. ΔT ($=T_s-T_r$) is related to the heat generated (or absorbed) by the sample in a unit time (dH/dt) when the sample undergoes an endothermic or exothermic reaction. It is frequently assumed that the DTA signal, ΔT, is proportional to the reaction rate -dx/dt, and is therefore governed by the same equations as DTG curves. This assumption, however, needs careful consideration. Usually one can assume that dH/dt is proportional to -dx/dt, but the proportionality of ΔT and dH/dt is only approximate.

In order to study the relation between the DTA signal and dH/dt, we have to make some assumptions concerning the heat flow in the experimental system. According to the model of Borchardt and Daniels [7]

$$dH/dt = C\, d(\Delta T)/dt + K\, \Delta T \quad , \qquad (2)$$

where C is the heat capacity of the sample and K is the heat transfer coefficient of the sample cell [3, p. 104]. Integrating Eq. (2) between t=0 and t=∞ gives the total heat of reaction (ΔH):

$$\Delta H = C(\Delta T_{t=\infty} - \Delta T_{t=0}) + K\int_0^\infty \Delta T dt \qquad (3)$$

Since at t=0 and t=∞ ΔT is 0, we get the simple equation

$$\Delta H = KA \quad , \qquad (4)$$

where $A = {}_0\int^\infty \Delta T dt$ is the area of the DTA peak. Since dH/dt is considered to be proportional to the reaction rate, one can see from (2) that -dx/dt is not proportional to ΔT but rather to $\Delta T+(C/K)d(\Delta T)/dt$. Actually, from (2) and (4) one gets:

$$-(dx/dt)\cdot A = \Delta T + (C/K)d(\Delta T)/dt \qquad (5)$$

The model of Borchardt and Daniels is based upon several strict assumptions. For example, C and K should be the same for the sample and the reference. However, more general models such as the model of Gray [8] yield similar results [3, p. 106].

C is the specific heat of the sample multiplied by its mass. For example, in 100 mg of a dilute solution, C=0.1 cal/deg. For a solid which obeys Dulong and Petit's law, the order of magnitude of C is 10^{-2} cal/deg, for a typical sample of 1×10^{-3} - 2×10^{-3} mole.

K can be estimated from DTA curves, using Eq.(4). From DTA measurements on $MgCl_2:6H_2O$ [9] and from various published results we concluded that typical values of K in modern systems are between 0.1 and 1 cal/deg·sec. Typical values of C/K in small samples are therefore between 10^{-2} and 1 (sec). In order to study the relation between the DTA signal and the reaction rate -dx/dt, several "computer peaks" were produced, assuming the equation

$$-dx/dt = Z\, x^{b} \exp(-E/RT) \qquad (1 \le b \le 2). \qquad (6)$$

The values of E were in the range 20 - 80 kcal/mole. Z values between 10^{15} and 10^{20} and a heating rate of 10 deg/min were assumed. For each set of the parameters E, Z and b, the reaction rate -dx/dt, as well as ΔT, were computed as function of the temperature, for the following values of C/K: 10, 1, 0.1, 0.01. Equation (5) as it is, cannot be used for calculations the DTA signal from the reaction rate, since $d(\Delta T)/dt$ is not known. However, one can exploit the fact that if

$$g(t) = h(t) + R\, dh/dt\ , \qquad (7)$$

than h(t) is given by the series:

$$h = g - R\, dg/dt + R^2 d^2g/dt^2 - R^3 d^3h/dt^3 + \ldots \qquad (8)$$

We found that in our case this series converges even for C/K values as large as 10. On each of these 'computer DTA peaks' we applied a best-fit algorithm which sought the parameters which optimally describe this peak in terms of eq. (6). An example is shown in Fig. 1. The parameters are: b=1, E=40 kcal, $Z=10^{15}sec^{-1}$, C/K=10 sec. The activation energy which was calculated from the ΔT curve (treating it as if it was the reaction rate) was E=39.52 eV, or 1.2% less than the original value of 40 kcal. For C/K=1, the maximal deviation of E from the original value was 0.5%, and for C/K=0.1 the deviation was no more than 0.1%.

CONCLUSIONS

From the discussion above one can learn that for a small sample and a reasonable heat transfer, methods of kinetic analysis which were developed for DTG can be used for DTA as well. Only for large samples and poor heat transfer, C/K is big enough so that the DTA signal is substantially different from -dx/dt. In this case the application of these methods of analysis to the ΔT signal may yield erroneous results.

A general method for the kinetic analysis of DTA peaks can be suggested on the basis of Eq. (5). First produce the curve of -dx/dt by numerically calculating the derivative of ΔT and then subtract (C/K)d(ΔT)/dt from the DTA signal, ΔT, at each point of the curve. The resulting -dx/dt curve can now be analysed by the standard methods of analysis which have been developed for DTG peaks.

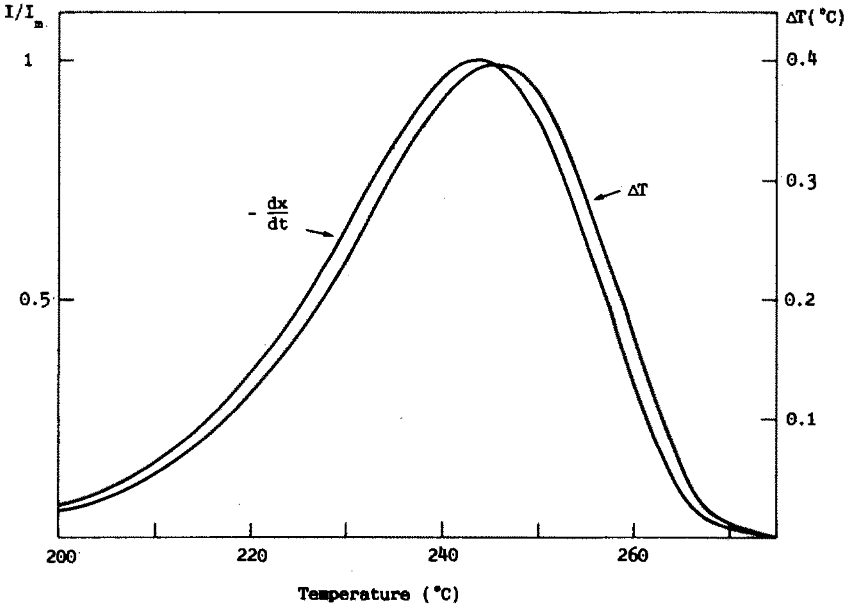

Fig. 1: The functions -dx/dt (left scale) and ΔT (right scale) as given by Eqs. (6) and (5), for b=1, E=40 kcal, $Z=10^{15}sec^{-1}$, C/K=10 sec.

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