PROCESSING OF THERMOANALYTICAL CURVES AND EXACT USE OF THERMAL ANALYSIS

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ABSTRACT

Equations for the correction of thermoanalytical signals are presented and the problem of the exact analysis of thermoanalytical curves is discussed.

It is surprising that in the Proceedings of the 8th ICTA Conference there is little information on the old problem of the difference between the obtained TA signal and the true course of processes in the material being heated.

When a sample of material is linearly heated, changes in its state occur. These changes can be expressed as the time dependence of some variable of state (Z) of the system under study:

$$Z = Z(t) \tag{1}$$

These changes are then detected by some detection system and a TA response (signal Y) is obtained as a function of time:

$$Y = Y(t) \tag{2}$$

Among the various classical TA methods, only two techniques exist whose signal (response) is linearly proportional to the actual time dependence of a variable of state, Z:

$$Z(t) = kY(t) + q \tag{3}$$

These are the well-known thermogravimetry (TG) and the more recent differential scanning calorimetry (DSC) in the compensation mode as realized in devices produced by Perkin-Elmer. In TG the variable of state Z is represented by the mass (m) or molar amount (n) of the sample under study:

$$m(t) = k_m Y(t) + q_m \text{ (g)}$$
$$n(t) = k_n Y(t) = q_n \text{ (mol)} \tag{4}$$

In the compensation form of DSC, the variable Z is replaced by the flux of the enthalpy (h) between the sample under study and its surroundings:

$$\dot{h} \equiv \frac{dH}{dt} = k_h Y(t) + q_h \; (\text{J s}^{-1}) \tag{5}$$

In other TA methods such as EGA (or EGD), DTA and DSC with heat-flux sensors, the TA response obtained is non-linearly distorted if we compare it with the true course of the process in the sample under study.

The distortion in EGA (EGD) is caused by a transport delay of the evolved gas. This is the reason for the difference between TG and EGD curves as reported by Bourrie and Filsinger [1]. In DTA (and heat-flux DSC), the cause of distortion is the thermal inertia of the sample with its holder.

Both of the above distortion effects were described several years ago. The thermal inertia effect can be evaluated if we start from the work of Faktor and Hanks [2], who set the energy balance equations for the DTA measuring head in 1967. The corresponding equation in the form

$$\dot{h} = \frac{dh}{dt} = \Delta C \phi - C \frac{d \, \Delta T}{dt} - K \, \Delta T \tag{6}$$

was presented by myself in 1973 at the calorimetric conference in Tbilisi and at the ICTA Conference in Budapest [3]. In this equation, $\dot{h}$ is the enthalpy flux, ΔT the temperature difference (DTA response), C the heat capacity of the sample (including its holder), ϕ the heating rate, $K = \text{f}(T)$ the apparatus constant and ΔC the difference in the heat capacities of specimens.

According to eqn. (6), the DTA signal consists of three terms:

$$\Delta T = - \frac{1}{K} \dot{h} - \frac{C}{K} \frac{d \, \Delta T}{dt} + \frac{\Delta C}{K} \phi \tag{7}$$

in which the first is proportional to the enthalpy flux, the second to the thermal inertia effect and the third expresses the change in the background (baseline) during heating, as indicated by Mackenzie in his Award Lecture at the 8th ICTA Conference. The mentioned equation (6) is suitable for converting the DTA signal, $\Delta T = \Delta T(t)$, into the true time dependence of the enthalpy flux, $\dot{h} = \dot{h}(t)$, as was verified by myself and my colleagues [4].

The transport delay effect in TA was, as far as I know, analysed by Vachuška [5] in 1978. It follows that the connection between the concentration [$c_v(t)$] of evolved gas detected in the detection cell at time t and the rate [$\dot{n}_v(t)$] of evolution of the gas in the sample holder is given, for a cylindrical outlet tube of diameter R and length L (from the heating area to the detector), by the equation

$$c_v(t) = \frac{R^4 L^2}{2 \dot{Q}^3} \int_{\tau=0}^{\infty} \frac{\dot{n}_v(t - \tau)}{\tau^3} \, d\tau \tag{8}$$

where $\dot{Q}$ ($\text{m}^3 \text{ s}^{-1}$) is the flux of the carrier gas. This equation can also be

used for the conversion of an EGA (or EGD) signal, $c_v = c_v(t)$, into the true time dependence of the rate of evolution, $\dot{n}_v = \dot{n}_v(t)$, using the computing procedure suggested at the National Conference TERMANAL 82 [6].

The situation is more complex if we want to convert the signal of ETA (emanation thermal analysis). The problem is connected with the absence of a variable of state whose change is the origin of ETA effects. Starting from information from Balek, I analysed this problem and proposed a new term, the escapability, ω, a variable defined as the mean probability that one atom of emanating gas will escape from the sample to the surroundings during 1 s (the unit of escapability is then s^{-1}). The relationship between the escapability, $\omega(\tau)$, and the ETA signal, $E(t)$, is

$$E(t) = K_E \sum_{i=\tau_0/2} \left\{ K_i \omega(t-i) \sum_{j=0} \left[\exp(-j\lambda) \prod_{k=0} (1 - \omega(t-i-k)) \right] \right\} \qquad (9)$$

where
$K_E = N_E \tau_0^2 \, [1 - \exp(-\lambda \, \Delta t/2)]$
$K_i \quad = \exp(-\lambda i)/i^3$
$\lambda \quad =$ decay constant
$\tau_0 \quad = \pi R^2 L/\dot{Q} =$ transport delay in the tube to the detector
$\Delta t \quad =$ time delay for the gas in the detector cell
$N_E \quad =$ emanation activity of the sample
$\dot{Q} \quad =$ flux of carrier gas
$R \quad =$ diameter of cylindrical tube
This equation can also be used [6] for computer processing of the ETA response curve to obtain the true time dependence of the escapability:

$$E = E(t) \to \omega = \omega(t)$$

It is thus apparent that any calculation of kinetic parameters from an original (uncorrected) EGA or DTA or heat-flux DSC curve is doubtful, in view of the existence of distorting effects connected with the principle of these methods. However, these effects can be removed by computer processing of the TA signal if we have more detailed information about the measuring head and sample (heat capacity) and the detection system (transport delay). By this means we can obtain the true time dependence of the sample behaviour under heating: however, there remains the question of how to process the obtained true (corrected) curve.

If we apply the normalization procedure to the true time dependence curve, we transform it into a "non-isothermal kinetic curve" in the integral form

$$\alpha(t) = \frac{Z(t) - Z_0}{Z_f - Z_0} \qquad (10)$$

or in the differential form

$$\frac{d\alpha}{dt} = \frac{dZ}{dt} \frac{1}{Z_f - Z_0} \tag{11}$$

where Z_0 and Z_f are the values of the variable of state before the start (Z_0) and after the completion (Z_f) of the process and α is the degree of conversion or advancement of the process.

Most thermoanalysts have started from the idea that the rate ($d\alpha/dt$) of the process can be expressed as a function of only two variables: the degree of conversion (α) and the temperature (T) in the form

$$-\frac{d\alpha}{dt} = A \exp(-E/RT)(1-\alpha)^n \tag{12}$$

where A, E and n are the pre-exponential factor, activation energy and order of reaction, respectively. Equation (12) represents a kinetic model that includes several simplifying assumptions. The acceptability (correctness) of these assumptions for heterogeneous processes is generally doubtful, as has been shown elsewhere [3,7,8]. In spite of these doubts, most simple TA curves are fitted reasonably well by this three-parameter model (12) with a correlation coefficient better than 90%, and the fitting could be even better if we used the four-parameter model as suggested by, e.g., Urbanovici and Segal [9]. The agreement between the model and simple TA curves is the reason for the widespread belief that we are able to determine the mechanism of a process by the evaluation of the parameters in the model (12) or in its variants. In fact, agreement of any three-parameter model with the monotonous smooth curve over a short temperature range does not imply success. Bekman of Moscow University used the following expression: "If I have three parameters (in the model), then I am able to draw an elephant. If I can use four parameters, then the elephant will wave his trunk".

The disagreement between the values of the kinetic parameters reported by diverse workers for a chosen process (e.g., for the dissociation of $CaCO_3$) confirms our scepticism regarding the usefulness of eqn. (12) for the determination of the mechanism of any heterogeneous process. Any progress in the evaluation of TA curves with regard to the mechanism of processes is connected with a less speculative approach starting from a deeper understanding of materials and their potential behaviour.

Such a promising approach can be seen in the excellent work of Jesenák presented in his plenary lecture, "Philosophy of the mechanism of diffusion controlled solid state processes" [10].

Other work important for the correct understanding of the shape of ETA curves was presented by Kříž et al. [11]. From their work follows the surprising result that the peak on an ETA curve does not necessarily need to be connected with any changes in the structure of the material.

It is unfortunate that at the 8th ICTA Conference there were few

contributions devoted to the exact use of thermal analysis. I assume that thermal analysis must be divorced from the speculative methods of formal non-isothermal heterogeneous kinetics to become a fully qualified part of science. I hope that the next ICTA Conference will be more successful in this field of activity.

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