Thermochimica Acta, 110 (1987) 87–93
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

METHODOLOGY OF STUDYING REACTION KINETICS BY THERMAL ANALYSIS

JAROSLAV KŘÍŽ

Paint Research Institute, Sokolovská 16, Prague (Czechoslovakia)

JAROSLAV ŠESTÁK

Institute of Physics of the Czechoslovak Academy of Sciences, Na slovance 2,
Prague (Czechoslovakia)

ABSTRACT

If thermal analysis is considered as a part of solid-state physics, inevitable problems of heterogeneity, transport phenomena, etc., occur. Even the recent oversimplified approach based on a primitive approximation of two independent, single-parameter functions is not without difficulty, particularly when readily available data-handling by computers is combined with an inadequate mathematical procedure. In addition, the apparatus response is worthy of analysis as the reaction rate is not always identifiable from changes in experimentally detected parameters.

INTRODUCTION

Thermal analysis is generally an exercise in solid-state physics and, as such, it has to deal with most of the difficulties in this field, namely the individuality of the structure under observation, the role of heterogeneity, transport phenomena, etc. In such a situation, thermoanalytical studies of kinetics have three possibilities: (1) to seek a more or less exact mathematical model of the physical process going on in the sample; (2) to give up all physical considerations and to look merely for a sufficiently flexible description function that could be fitted to most of the experimental curves; and (3) to be restricted to very simple approximations as usually used for engineering purposes or process optimization.

In the first instance, we usually encounter serious difficulties even when formulating the model, not to mention the curve-fitting problem, which may be tedious even on a medium-sized computer. In the second instance, only a different form of data storage is obtained, which can have some merit but is

---

Thermal Analysis Highlights, 8th ICTA, Bratislava, Czechoslovakia.

devoid of any physical meaning. In the third instance, we obtain some physical meaning from the results without being sure they really make sense; however, we can easily handle these simple functions, sometimes even manually. This seems to be the reason for their general attractiveness as popularized in early kinetic studies (cf., ref. 1). Some recent investigations have indicated, however, that even here some difficulties arise, particularly concerning the applicability of mathematical models describing the kinetics of non-isothermal heterogeneous processes, if [1,2]: (1) they are derived for homogeneous-like systems (i.e., the common concept of reaction order); (2) they are derived under isothermal conditions (equations named classically after individual authors such as Jander, Avrami and JMAKY; (3) they are not desensitized by mathematical treatment (e.g., popular logarithmization); and (4) they overlap each other (diffusion with phase-boundary reactions, individual forms of nucleation–growth equations in their integral forms).

GENERAL APPROACH

To outline the situation in broad terms, let us consider that we measure some integral effect Θ, which is some function of the conversion of physico-chemical processes going on in the sample, of temperature T, and at time t, i.e.,

$$\Omega\Theta = \int_v \Phi(\{\alpha_i(x)\}T(x)t)\,\mathrm{d}x \tag{1}$$

where the operator Ω is mostly $\partial/\partial t$, Φ is some function (the integral of which is taken over the whole volume), x is the general coordinate and $\alpha_i(x)$ is the conversion of the ith process at the point x. In most practical studies only a single process is considered, which is certainly an oversimplification [3]. Additionally, both α and T are considered to be independent of x, i.e., material and energy transport are ignored, the underlying idea being that some mean value of α and T can be considered. However, there are some doubts about this; for example, the temperature measured at one point is freely attributed to the weight loss effective at the surface, which is evidently far from the ideality. In fact, the transport equation

$$\partial\theta(x, t)/\partial t = \nabla[\kappa\nabla\theta(x, t)] + \eta(x, t) - \zeta(x, t) \tag{2}$$

(where θ is either the temperature or concentration of the transported species, κ is the transport coefficient and η and ζ are the source and ditch functions, respectively) should be contained in our model in some way. Zajanchovski and Dambelkane [4] argued that heat transport should be considered in the analysis of a derivatographic experiment. This is certainly not a new idea but, nevertheless, is a valuable one. Unfortunately, they failed to demonstrate by simulation and/or experiment the net effect of the experimental conditions and thus the heat transport can have a value as constants obtained by analysis. Actually, the only method in which Θ is connected with α in a simple manner is DSC and, with some qualification, TG or some electromagnetic measurements, but certainly not DTA, EGD or ETA. DTA, however, is the only method in which the deviation of the temperature from the programmed and so far idealized value (frequently taken for our kinetic evaluations) is clearly exhibited [5].

SIMPLIFIED APPROACH

Most thermoanalysts, however, seem unconcerned by eqns. (1) and (2). The direct correspondence of Θ with α, the use of the mean values of α and T, the idealized course of T and, in addition, the general belief of the separability of α and T, namely the form of expressing the reaction rate $\dot{\alpha} = (\mathrm{d}\alpha/\mathrm{d}t)$ [6,7]:

$$\dot{\alpha} = k(T)\mathrm{f}(\alpha) \tag{3}$$

is almost a dogma in routine kinetic analysis. All this leads to complicated questions; however, leaving all aspects of energy transport aside, the simple fact of self-cooling and/or self-heating due to reaction heat absorption and/or production is worthy of consideration because T and α become really interdependent. Also, the Arrhenius form of the rate constant, $k(T) = K_0 \exp(-E/RT)$, is accepted without question, which is justified only for a random distribution of energy states, i.e., the Boltzmann distribution [8]. Let us take an ideal crystal with its vibration modes as an example of other possibilities. It has been known for some time that using these relationships, the so-called kinetic compensation effect [8–10] is observed in the kinetics of many solid-state reactions. In general, this effect consists of an overt linear dependence between ln K_0 and E or, in other words, in the uncertainty of the actual values of both quantities. After some heated debate, it seems to be agreed that the main cause of the relationship [10]

$$\ln K_0 = a + bE \tag{4}$$

may be the mathematical form of the Arrhenius equation or, using the Arrhenius equation, the change in ln K_0 will have an analogous effect on the curve shape/position to that of E, clearly demonstrated as early as 1966 [11]. This mathematical fact cannot be removed by any type of kinetic treatment or evaluation procedure; there are, however, ways of minimizing its adverse effect, often re-examined during the past 20 years. One of the most promising approaches is the normalization of the Arrhenius equation by introducing the centred temperature T_0 to hold $k(T) = K_0 \exp[-E/R(T - T_0)]$ [12–14]. The above equation was entered from a slightly new angle by Levchik et al. [15]. Starting from geometrical and statistical considerations, they illustrated their earlier method of obtaining invariant parameters consisting of a suitable transformation of variables. Equation (3) suggests, for easier work, the linearization $\ln \dot{\alpha} = \ln K_0 - E/RT + \ln(\mathrm{f}(\alpha))$ [6,7,9,16]. Vyazovkin and Lesnikovich [17] argued, however, that such a procedure reduces the sensitivity of the analysis to the variation of $\mathrm{f}(\alpha)$ and, as a consequence, to the difference between various mechanisms, as is well known [1,5,16]. Such a poor sensitivity, however, seems to apply even to non-linear regression analysis. This appears to be especially the case in the common least-squares method. Here, we minimize the function

$$\chi = \sum_{i} \left\{ \alpha_{i,\mathrm{exp}} - F\left[\frac{K_0}{\phi} \int_{T_0}^{T} \exp(-E/RT)\, \mathrm{d}T \right] \right\}^2 \tag{5}$$

where $\alpha_{i,\mathrm{exp}}$ is the experimentally obtained conversion at the ith point, ϕ is the heating rate and F is the obvious transform of $\mathrm{f}(\alpha)$ in eqn. (3). Extensive work has been carried out on the numerical aspects of this, and efficient computer programs have been devised in various laboratories. In our opinion, one of the most reliable algorithms seems to be the Fortran procedure FUMILI, which is a co-product of nuclear scientists in Dubna (U.S.S.R.) and CERN (Switzerland) and is available in several computer libraries. Naturally, in any optimization procedure there arises the problem of experimental errors. At this conference, Militký and Čáp [18] considered this problem in greater detail regarding the additive and multiplicative errors in the experimentally established values of the Arrhenius $k(T)$. They suggested an improved method of parameter estimation that maximizes their reliability by means of power transformation.

COMPUTER ANALYSIS AND MATHEMATICAL TREATMENT

The use of computers is, however, far from common in routine thermoanalytical work as yet. This is why new studies dealing with more direct methods of curve characterization and parameter estimation continue to appear. Pokol et al. [19], for example, simulated the course of eqn. (3) with the simple function $\mathrm{f}(\alpha) = (1-\alpha)^n$ and found an almost linear dependence of the DSC peak position and the width parameter on the activation energy for given K_0 and n. With everything else fixed, changes in K_0 lead to a moderately curved plot, changes in n leaving the position almost unaffected but having a pronounced effect on the width. These results, which are in agreement with those of Kříž [20], can thus be used for the first estimation of the parameters provided that the master equation holds. Varhégyi et al. [21] considered the asymmetry of the curve, this time for TG, its criterion being chosen in a rather random manner; this idea has value if not novelty. By characterizing the curve shape by a small set of suitably chosen parameters before any detailed analysis, we may be able to exclude all irrelevant mathematical models (mechanisms), thus avoiding wastage of computing time. Another approach is that of Horsåk and Šesták [22], using a modified exponential function to fit both branches of a DTA peak to look for changes in associated (characteristic) constants in relation to changes in the mechanism of the rate-controlling physico-chemical process. There is, however, an important difference between the analysis carried out manually and that carried out on a computer. In manual work, we can probably trust ourselves to be able to establish the shape parameter from one or two points. In a computer analysis, even moderate experimental errors can cause a disaster in this respect; therefore, more collective criteria of the curve shape should be chosen. Regarding the curve formally as a distribution, for instance, the first four of its moments, the ith moment being defined as

$$\mu_i = \int_{-\infty}^{+\infty} T^i \, \mathrm{d}\Theta(T) \tag{6}$$

seems to be sufficient to express most of its important features. It is well known that the first moment gives the position of the most important part of the curve (mean value), the second its width (dispersion) and the third and fourth the more elusive shape properties. For a computer treatment, the discrete analogy of eqn. (6) may be more appropriate as

$$\mu_i = \sum_j T_j^i \, \Delta\Theta_j / \sum_j \Delta\Theta_j \tag{7}$$

To summarize the above considerations, we appear to have a number of moderately efficient algorithms for curve fitting either by computer or even manually. The weak point seems to be the common set of master equations that we use as the mathematical models. Their forced simplicity reflects the situation as it had been before the advent of computers and cannot be fully justified today. Hence, further theoretical work is called for in thermal analysis.

DISCUSSION

As shown above, the mathematical treatment of the kinetic analysis of thermoanalytical data is still far from being appropriate to the non-steady type of experimentation. There arise, however, some additional complications not mentioned yet, particularly the response of the entire apparatus to the process in question. Assuming a simplified decomposition process, neglecting possible adverse effects due to physico-chemical events within the sample and its surrounding gaseous envelope, the experimentally detected change in a physical parameter (selected to represent the reaction under study) must not be generally identified with the reaction rate required for further kinetic evaluations (see eqn. (3)). The desired direct proportionality can be roughly assumed for the thermogravimetry of daltonides (at constant stoichiometry of phases) but not far the case of popular DTA where, in fact, the measured (ΔT_{DTA}) and controlled (T_{CON}) quantities interfere with each other ($\Delta T_{\mathrm{DTA}} \approx T_{\mathrm{CON}} - T_{\mathrm{SAMPLE}}$), complicating the proportionality by the effect of heat inertia [5,23]:

$$\dot{\alpha} = -\Delta\dot{T}_{\mathrm{DTA}} c_P/\Delta H - \Delta T_{\mathrm{DTA}} K_{\mathrm{DTA}}/\Delta H + K(\phi,\ K_{\mathrm{DTA}},\ c_P) \tag{8}$$

where c_P, ΔH, K_{DTA} and K are heat capacity, enthalpy change, heat transfer coefficient and parameter (constant) function, respectively. Another case is that of DPA (differential pressure analysis), where the dependence of the pressure difference between the chambers containing the sample and the reference, ΔP, is monitored. Here the interdependence between the pressure and temperature (equilibrium background of the reaction) must be considered, so that [24]

$$\dot{\alpha} = (\Delta\dot{P}T - \Delta P\dot{T})(T_\infty/P_\infty)/T^2 \tag{9}$$

A still different case is the measurement where the reaction chamber (x) and the detector (x_s) are separated by a connecting tube (length $h = x - x_s$ with a mean flow rate of the carrier gas v). The overall volume V of gas entering the detector in the time interval from t to τ (time delay equal to $h/2v$) must be assumed [25] to provide a reaction rate roughly proportional to the sum of acceleration $[\ddot{v}(\tau - \mathrm{t})/(V_\infty - V_0)]$ and rate $[\dot{v}(V_\infty - V_0)]$ terms. Neglecting diffusion, however, can advance the zone by a factor of two. The correct equation for solving the transport problem in general is very complex [26]:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} + \sigma(x - x_s)\frac{\epsilon(\alpha,\ T,\ t)}{V} \tag{10}$$

requiring a solution by the method of Green functions, which is too complicated for everyday use. The explicit form then depends on the source function $\epsilon(\alpha,\ T,\ t)$ and Dirac function $\sigma(x - x_s)$ boundary conditions and provides the concentration profile $c(x,\ t)$ necessary for solving the conversion α and its rate $\dot{\alpha}$.

REFERENCES

1 J. Šesták, J. Therm. Anal., 16 (1979) 503.
2 J. Šesták, in Thermal Analysis, Proc. 6th ICTA, Vol. 1, Birkhauser Verlag, Stuttgart, 1980, p. 29.
3 J. Kříž, Thermochim. Acta, 57 (1982) 13 and J. Therm. Anal., 15 (1979) 325.
4 Z. Zajanchkovski and M. Dambekalne, 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 81.
5 J. Šesták, Thermochim. Acta, 98 (1986) 339.
6 J. Šesták, Thermophysical Properties of Solids, Elsevier, Amsterdam, 1984.

7 E. Koch, Non-isothermal Reaction Analysis, Plenum Press, New York, 1978.
8 P.D. Garn, in Thermal Analysis, Proc. 5th ICTA, Heyden, London, 1977; J. Therm. Anal., 7 (1975) 588; 13 (1978) 581.
9 P.D. Garn, Thermoanalytical Methods of Investigation, Academic Press, New York, 1964.
10 J. Szako, J. Therm. Anal., 9 (1976) 101; 8 (1975) 593.
11 J. Šesták, Talanta, 13 (1966) 567.
12 J. Militký, Modelling of Non-isothermal Processes, Rep. VÚZ, Dvůr Králové n/L 1979; Proc. TA and Calorimetry of Polymers, ČSVTS Silon, Planá n/L 1979, p. 13 (in Czech).
13 J.J. Pysiak, in Thermal Analysis, Proc. 6th ICTA, Vol. 1, Birkhauser Verlag, Stuttgart, 1980, p. 35.
14 V.A. Logvinenko, Kinetics of Coordination Compounds, Academy of Sciences, Novosibirsk, 1983 (in Russian); J. Therm. Anal., 10 (1976) 363.
15 S.V. Levchik, G.F. Levchik and A.I. Lesnikovich, 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 157.
16 N.A. Chernova, I.V. Archangelski and L.N. Komissarova, J. Therm. Anal., 13 (1978) 315; 18 (1980) 347.
17 S.V. Vyazovkin and A.I. Lesnikovich, 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 161.
18 J. Militký and J. Čáp, 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 77.
19 G. Pakol, S. Gál and E. Pungor, 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 89.
20 J. Kříž, unpublished results.
21 G. Várhegyi, P. Szabó and F. Till, 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 141.
22 I. Horsák and J. Šesták, unpublished results.
23 J. Šesták, P. Holba and G. Lombardi, Ann. Chim. (Rome), 67 (1977) 73.
24 P. Holba and K. Tobola, in Termanal '79 (Proc. Czech. Conf. TA), SVŠT, Bratislava, 1979, p. 43 (in Czech).
25 J. Vachuška, in J. Šesták (Ed.), Methods of TA Curves Evaluation, DT ČSVTS, Prague, 1978, p. 23 (in Czech).
26 J. Kříž, Thermochim. Acta, submitted.