Special Review

PROBLEMS OF NON-LINEAR THEORY IN DIFFERENTIAL SCANNING CALORIMETRY

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The problems of DSC non-linear theory, connected with the dependence of the thermophysical parameters upon the temperature, are discussed. The changes in thle form of the thermal energy curve recorded by the device as results of the thermaconductivity jump and heat capacity shift taken into account in the course of transformation are shown. A correct non-linear DSC model is formulated. The mather matical apparatus and some simplifying notions for calculation with the non-lineamodel are suggested. The interpretation of a calorimetric curve of an adiabatic scan. ning microcalorimeter over a pretransition range of temperatures is given as an example

The theory of any method of measuring involves at least two aspects. One of them is related to the problems of designing a device, whereas the second deals with the interpretation of the results obtained. It is to some problems of the latter aspect that our study is devoted, in particular to non-linear effects and non-linear theory in scanning calorimetry.

In 1963–64 there appeared an original thermal method of physico-chemical investigations – differential scanning calorimetry (DSC), based on an entirely new principle of measurement, *viz.* by recording thermal energy compensating temperature imbalance in the cells [1, 2]. The development and successful exploitation of the corresponding calorimeters proved them to be of great promise in solving a number of problems [3, 4].

However, the rapid introduction of new complex methods of analysis results in a large amount of new and highly promising information, and the fact that the use itself and development of the method pass through a number of stages is sometimes ignored. Any method, especially a universal one, is sure to pass through the phase of a simplified interpretation. The possibilities of this stage being exhausted, the method should either be further developed or turn from being a method principally giving new information into a routine laboratory one. The latter fact is evidence of a limited power and peculiarity of the method.

All this concerns both the problem of device designing and to a greater extent the problem of interpretation of the results of measurement. It often happens that the possibilities which good, high-grade equipment might give become negligible because of imperfect interpretation.

From our point of view, approximately the same intermediate situation can be seen in the use of DSC, especially when this method is applied for kinetic and thermophysical investigations. On the one hand, highly-sensitive apparatuses have been developed, and on the other there exist a number of well-developed model representations [4, 5] for interpretation of the experiment. This might seem good at first glance. However, the trouble is that the theoretical models are too idealized and far from the real experiment conditions.

Anomalies in the behaviour of thermophysical parameters with temperature. DSC theory with thermal conduction jump an heat capacity shift taken into account

The main feature of modern DSC theory is the linearity of the models under consideration. In fact, due to the functional, very often considerable dependence of the thermophysical parameters on temperature, the correct model must be essentially non-linear. It is well known that the heat capacity C greatly depends on temperature T, especially in the pretransition region. Figures 1 and 2 show typical anomalies in the behaviour of specific heat capacity with temperature for neptunium dioxide [7] and polytetrafluoroethylene [8].

The data on the dependence of thermal conduction λ upon the temperature are less known and not so numerous. The curves of λ changes for natural and vulcanized rubber are given in Fig. 3. In the authors' view, the thermal conduction jumps correspond to the phase transitions denoted by the arrows [9, 10], but it was not possible to measure them directly. All the curves $\lambda(T)$ prove to be of the same specific shape, having a sharper slope at high temperatures. Figures 2 and 4 give λ data [8] for polytetrafluoroethylene and phenol-formaldehyde resin. The corresponding results speak in favour of sharp changes in the phase transformations of both the heat capacity and the thermal conduction of the substances under investigation. A great dependence of λ on T in the definite temperature ranges is characteristic of different porous and composite materials, especially those containing moisture, even when no transformations take place.

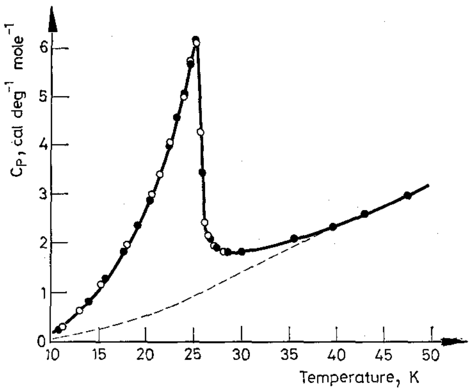

Fig. 1. Anomaly of neptunium dioxide heat capacity

To illustrate the changes caused by the dependence of thermophysical parameters on the temperature, let us consider the modern DSC theory for the sharp transitions [5], having introduced for simplicity only the thermal conduction jump and the shift of the specific heat capacity during the transformations. In accordance with [5] we shall consider that the calorimeter cell (Fig. 5) can be represented by the isothermal platform at the temperature T_p, which is connected with the temperature source T_s via the equivalent thermal resistance R and the

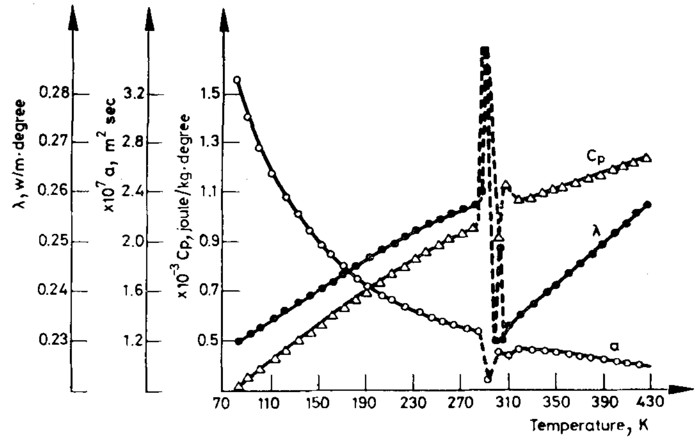

Fig. 2. Thermophysical properties of polytetrafluoroethylene

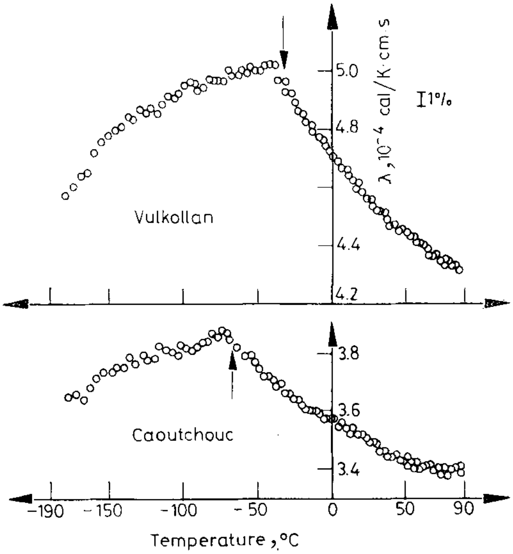

Fig. 3. Heat conductivity of natural and vulcanized rubber

heat flow meter A, where T_s changes linearly with the speed Φ. The sample, representing a flat homogeneous slab, is in ideal thermal contact with the platform. The equivalent scheme of such a cell is shown in Fig. 6.

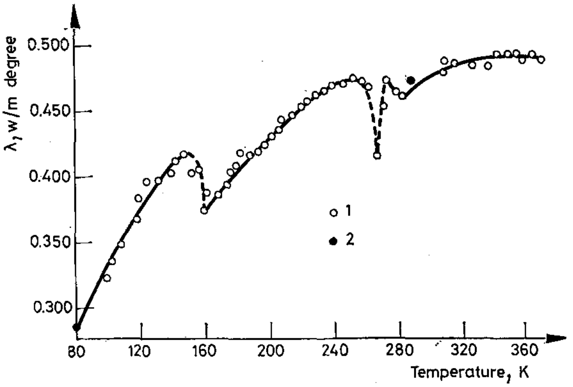

Fig. 4. Heat conductivity of phenol-formaldehyde resin with glass fibre

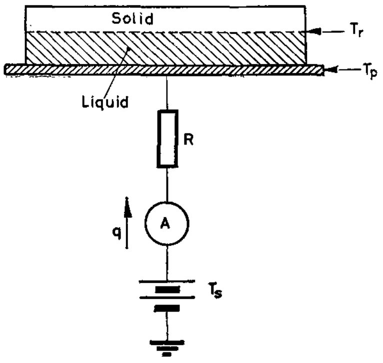

Fig. 5. Block-scheme of DSC cell

T_r denotes the transition reaction temperature, and x the thickness of the sample layer which undergoes transformation (a liquid phase). Thus, on the basis of three expressions:

$$q = S\rho\eta\frac{dx}{dt} + \Delta C\rho S\Phi x\,;$$

$$q = \frac{S(T_p - T_r)}{rx + \Delta r\delta}\,; \qquad q = \frac{T_s - T_p}{R}$$

it is possible to derive the following differential equation for the thermal energy:

$$\rho\eta(RS + \Delta r\delta + rx)\frac{dx}{dt} + r\Delta C\rho\Phi x^2 + \Delta C\rho\Phi(RS + \Delta r\delta)x = \Phi t \tag{1}$$

where S, r, $\Delta r\delta$, ΔC and ρ mean the area, the thermal resistance, the jump of the thermal resistance, the shift of the specific heat capacity and the sample density, respectively; η is the heat effect per unit weight of the substance; and t is the time.

Let us consider two limiting cases:

$$\text{a) } \Delta C = 0;\ \Delta r\delta \neq 0 \qquad \text{b) } \Delta C \neq 0;\ \Delta r\delta = 0$$

It is clear that in case a) the solution of Eq. (1) will be as follows:

for the instrumental limitation ($R \to \infty$):

$$q = \frac{\Phi t}{R} = q_N \tag{2}$$

where q_N is the thermal energy in accordance with the O'Neil theory [5];

for limitation by the sample ($R \to 0$):

$$q = \frac{S\Phi t}{\Delta r\delta \sqrt{1 + \dfrac{r\Phi t^2}{\rho\eta\Delta r^2\delta^2}}} \tag{3}$$

In case b), when $R \to \infty$:

$$q = q_1 = \frac{\eta}{R\Delta C}\left[1 - \exp\left(-\frac{\Delta C\Phi t}{\eta}\right)\right] \tag{4}$$

at small t:

$$q_1 = \frac{\Phi t}{R} = q_N \tag{5}$$

at large t:

$$q_1 = \frac{\eta}{R\Delta C} = q_N \frac{\eta}{\Delta C\Phi t} \tag{6}$$

When $R \to 0$:

$$q = q_2 = \frac{S\eta\left[1 - \exp\left(-\dfrac{2\Delta C\Phi t}{\eta}\right)\right]}{2\Delta Cr\sqrt{(\rho r)^{-1}\left[\dfrac{t}{\Delta C} - \dfrac{\eta}{2\Phi\Delta C^2}\left(1 - \exp - \dfrac{2\Delta C\Phi t}{\eta}\right)\right]}}, \tag{7}$$

at small t:

$$q_2 = S\sqrt{\frac{\rho\eta\Phi}{r}} = q_N; \tag{8}$$

at large t:

$$q_2 = \frac{S\eta}{2}\sqrt{\frac{\rho}{\Delta Crt}} = \frac{q_N}{2}\sqrt{\frac{\eta}{\Delta C\Phi t}} \tag{9}$$

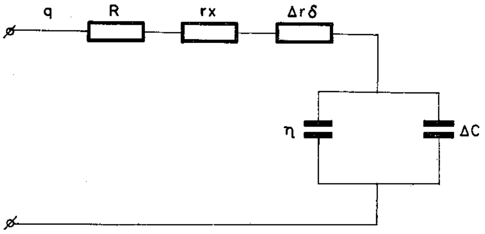

Fig. 6. Equivalent scheme of DSC cell

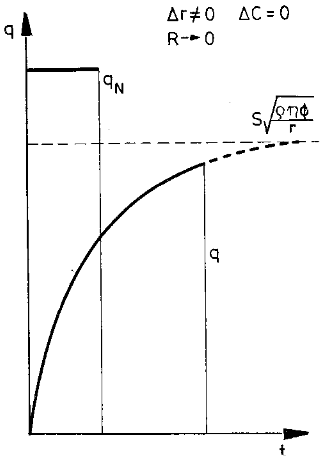

Fig. 7. Heat power dependence upon time in DSC for the case of limitation by the sample. q_N — according to O'Neil's theory; q — taking into account heat conductivity jump

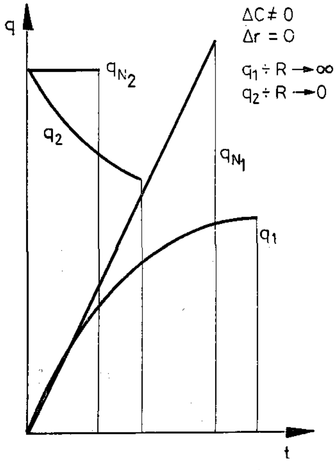

Fig. 8. Heat power dependence upon time in DSC, $q_{N_{1,2}}$ for $R \to \infty$; and $R \to 0$ according to O'Neil's theory respectively; $q_{1,2}$ for the same cases taking into account the shift in specific heat capacity

On the basis of Eqs (2) and (5) it follows that the thermal conduction jump does not influence the results of the theory in the case of the instrumental limitation. It is only at large t that the shift of the specific heat capacity appears. One should bear in mind, however, that when R is large the situation cannot be of much interest, as in such a case the properties of the sample and the character of the transition in it are eliminated completely. In this meaning the case of limitation by the sample is more informative from the practical point of view. From expressions (3) and (9) it follows, however, that with $R \to 0$ the behaviour of q differs noticeably with time from the one predicted by O'Neil's theory. In Figs 7 and 8 the corresponding relationships for q and q_N are represented. In Fig. 9 the thermal absorption curve is given, taking into account both the thermal conductivity jump and the specific heat capacity shift of the sample on transformation.

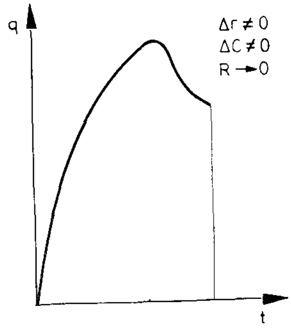

Fig. 9. Heat power dependence upon time for the case of limitation by the sample taking into account both heat conductivity jump and specific heat capacity shift

Thus, taking into consideration the anomalies in behaviour of λ and C in phase transitions results in an appreciable change of the curve form of the recorded thermal energy. Thus, for instance, for chymotrypsinogen [11]

$$\Delta C \simeq 0.15 \frac{\text{cal}}{\text{g} \cdot \text{degree}}, \qquad \eta \simeq 2-6 \frac{\text{cal}}{\text{g}} \text{ (depending}$$

on the pH), and the transition temperature range is approximately 20°. It follows that the contribution, for example, of the exponential term in expression (7) will differ from 1 (according to O'Neil) by a value exceeding 30%.

Analytical expression of the dependence of thermophysical parameters on temperature. Non-linear model of DSC

Unfortunately, in the publications up to now there are not to be found any strictly-based recommendations on the character of thermophysical parameter changes in the course of transitions. For this reason, to decide this problem the authors will have to resort only to a formal description [12] based on the experimental data. In this case one can follow two paths.

The first method is based on introduction of empirical relationships of $C(T)$ and $\lambda(T)$. It is known [13] that in second-order phase transitions the specific heat capacity has the appearance of a λ-like function (Figs 1 and 2). It is for this reason that the temperatures corresponding to such transitions are often called λ points. In their turn, λ-curves can be approximated fully enough by an expression such as

$$C(T) = C_0 + A_c(T - T_0) + \frac{B_c + D_c T^{s+1}}{T^s} \exp\left(-\frac{\phi}{RT}\right) \tag{10}$$

where A_c, B_c, D_c and s are some constants, and ϕ may sometimes be associated with the energy of new phase formation (point defect).

In this expression the peak corresponds to changes in specific heat capacity in connection with a phase transition, and linear segments correspond to ordinary temperature variations before and after the transformation.

In the case of first-order phase transitions, C_p tends to infinity. This means that the transformation from one phase into another takes place with a jump. In their turn, the necessary conditions for this jump are the absolute purity of the substance and its homogeneity. The presence of impurities, various microdefects, structure heterogeneity, bonding with solvent, etc. finally all result in extension of the phase transition over some temperature range. Further, it is quite evident that any instrument, on account of inertia inherent to it, responds to any instantaneous transformation with some delay, and this is also one of the reasons why the extension takes place. Therefore, even without taking into account the phenomena of premelting, C_p appears practically to be some finite function of T (Fig. 1). Thus, considering the real situation, in this case as well one should think it expedient to represent approximately the dependence of $C_p(T)$ in terms of some extreme asymmetric function T like that of (10).

In this way the suggested method allows one to describe the influence of phase transitions of types I and II on the temperature of the sample uniformly, the transitions differing both in function amplitude $C_{p,v}(T)$ and in the asymmetry magnitude.

Thermal conductivity usually changes in direct relation or in inverse relation with heat capacity (Fig. 2). For this reason the function $\lambda(T)$ may be described as well as for $C(T)$ by the expression

$$\lambda(\mathrm{T}) = \lambda_0 + A_\lambda(T - T_0) + \frac{B_\lambda + D_\lambda T^{s+1}}{T^s} \exp\left(-\frac{\phi}{RT}\right) \tag{11}$$

The second method is based on the property of additivity of the heat capacity of the system. If, for example, the first-order phase transition takes place, the total heat capacity of the sample at any separate moment may be written as a sum [3]:

$$C = C_2\alpha + C_1(1 - \alpha)$$

where α is the extent of conversion and C_1 and C_2 are the heat capacities of the sample before and after conversion, respectively. The disadvantage of this method is that it is fully applicable only to invariant heterogeneous transformations. For second-order phase transitions or chemical reactions, such a description either does not apply at all or appears irrational. Of course, in a number of situations one could get satisfactory results by taking C_1 and C_2 as functions of temperature or time. But finally in such a case we would come to the first variant. There is another important thing one should not forget. The thermal conductivity coefficient has no property of additivity and because of this cannot be characterized by means of the second method.

Summing up the considerations of the two methods of analytical description of the behaviour of C and λ in the course of transitions, it should be admitted most expedient to represent these parameters in the form of empirical temperature relationships.

Taking into account expressions (10) and (11), the non-linear mathematical model of DSC may be formulated in the following way:

$$C_i(T_i)\rho_i \frac{\partial T_i}{\partial t} = \frac{\partial}{\partial x}\left[\lambda_i(T_i)\frac{\partial T_i}{\partial x}\right] + \frac{K}{x}\lambda_i(T_i)\frac{\partial T_i}{\partial x} \pm (i-1)\,\Delta H\frac{\partial \alpha}{\partial t}\;; \tag{12}$$

$$\frac{\partial \alpha}{\partial t} = f(\alpha)Z\exp\left(-\frac{E}{RT_2}\right)\;; \tag{13}$$

$$C_i(T_i) = C_{io} + A_{ci}(T_i - T_0) + \frac{B_{ci} + D_{ci}T_i^{s+1}}{T_i^s}\exp\left(-\frac{\phi}{RT_i}\right) \tag{14}$$

$$\lambda_i(T_i) = \lambda_{io} + A_{\lambda i}(T_i - T_0) + \frac{B_{\lambda i} + D_{\lambda i}T_i^{s+1}}{T_i^s}\exp\left(-\frac{\phi}{RT_i}\right) \tag{15}$$

$$\rho_i = \rho_i(t); \qquad T_i(x,0) = T_0 \tag{16}$$

$$\lambda_i(T_i)\frac{\partial T_i}{\partial x}\bigg|_{x=0} = q_i(t)\;; \quad \lambda_i(T_i)\frac{\partial T_i}{\partial x}\bigg|_{x=\Delta} = q(T_i) \tag{17}$$

$$i = 1,2; \qquad K = 1,2,3.$$

$$T_1 \equiv T_2 \tag{18}$$

$$\text{DSC:}\ q_i(t) = q_{io} \pm \delta q_i(t);$$

$$q(T_i) = \sigma(T_i^4/_{x=\Delta} - T_{out}^4);$$

$$\text{ADSC:}\ q_i(t) = q_{io} \pm \delta q_i(t);$$

$$q(T_i) = 0$$

where T_i is the temperature in the reference cell ($i = 1$) or in the sample cell ($i = 2$); T_{out} is the outside temperature; C_i, λ_i and ρ_i are the specific heat capacity, thermal conductivity and density of the sample and of the reference, respectively;

x is a coordinate; t is time; α is the extent of conversion; $f(\alpha)$ is a function characterizing the order of the reaction; Z is a pre-exponent; E is the energy of activation; σ is a radiation coefficient; q_{i_o} is the density of constant heat flow; δq_i is the density of heat flow compensating for temperature imbalance in the cells; Δ is the thickness of the substance layer or solution in the case of a flat cell ($K = 0$) and the radius of cylindrical ($K = 1$) or spherical ($K = 2$) cells; and ΔH is the latent heat of conversion in the case of a first-order phase transition and the heat effect in the case of a chemical reaction.

If a reference is thermoinert, then $B_{c1} = D_{c1} = B_{\lambda 1} = D_{\lambda 1} = 0$. An important feature of the formulated model is that it suggests variations in density of the substance under investigation depending on time. This is a very important fact, especially when the transformations take place with the evolution of a gaseous phase.

Note 1. First-order phase transitions usually correspond mathematically to Stephan's problem. It is known, however, that solution of such problems causes some difficulties. And if one takes into consideration the fact that both C and λ change greatly with temperature before and after the transition, all the difficulties and practical failure of such attempts become quite clear. Therefore, the authors think expression in the form of the system (12)–(18) to be more preferable. Further, taking into account that this allows us to cover all types of transformations by means of one and the same model, the preference of such an approach becomes even more evident.

Note 2. Unfortunately, at present nothing is known about changes in heat capacity and thermal conduction in the course of chemical reactions.

It is not probable that they would differ greatly from corresponding variations on phase transitions. Thus, the mode of recording of functions $\lambda(T)$ and $C(T)$ is also preserved in the case of irreversible conversions. This is also favoured by the circumstance that both C and λ include a number of constant coefficients determined from the experimental data.

The latter allows one to modify to a great extent corresponding functional dependencies.

Mathematical apparatus

In order that the mathematically very complex non-linear model formulated by us should prove to be fruitful, it was necessary to find methods of solving partial differential equations which would be effective enough for application to the analysis of thermal behaviour in comparative calorimetry.

It should be taken into account that they must be not only simple enough, but also accurate. It was established, however, that such a universal method does not appear to exist. Nevertheless, two methods are near to it – the integral one [14] and the Kantorovitch method [15]. The former method is rather simple, but not sufficiently accurate. The latter has good accuracy under conditions of the correct choice of basic functions, but this is not always easy to do.

One may choose the integral method as the basic mathematical procedure because of the two following circumstances. Firstly, this method, as a rule, leads to a great error for small Fourier number values, when the heat process is not established. Taking into consideration that the DSC measurements are usually carried out long after switching on the warming-up, it is possible to assume the temperature distribution in the cells to be quasi-stationary. And in this case, the integral method gives quite acceptable accuracy. Secondly, as will be seen later, the energy characteristics of the processes under investigation are of great interest (e.g. the energy of compensating heat flow). The integral method, in its turn, being virtually a mathematical interpretation of the heat flow conservation law, proves to be accurate with reference to the latter. Therefore, when we speak about the use of energy functions for determining some characteristics of physico-chemical transformations, rather good results may be expected from the integral method.

In short, the essence of this method is as follows [12]: The solution of a one-dimensional non-stationary heat-conduction equation is searched for in the form of some function of coordinate x and time t. (For example, x is a polynomial

$$f_1(T)\frac{\partial T}{\partial t} = \nabla\,[f_2(T)\nabla T] \tag{19}$$

with unknown coefficients $a_i(t)$, depending on t.) All $a_{i\neq k}(t)$ are expressed from boundary conditions through one coefficient $a_{i=k}(t)$. The expression obtained for the temperature is substituted into the conduction equation. Both parts of the latter are multiplied by a form coefficient and integrated with respect to x within the boundaries. As a result, one has a common differential equation for $a_{i=k}$, which is solved in a usual way. After determining $a_{i=k}$, the rest of $a_{i\neq k}$ are easily found by means of expressions determined before.

We have worked out two forms of the combined method of solution of non-linear partial differential equations, specially for the cases with increased demands as to the accuracy [12]. The first of these forms combines the advantages of the Kantorovitch method and the integral one. Moreover, the latter is used on the one hand as a basis for developing basic functions according to the former, and on the other hand as a starting zero approximation. As a result of this, the accuracy of solution in the first approximation increases as compared to the results of the integral method. The answer is in the form available for any t, so it is not necessary to introduce the concept of "thermal layer", and, consequently, to determine and coordinate two different expressions for temperature. The characteristic feature of the proposed method is the possibility to make the solution obtained more precise.

For one-dimensional problems, the essence of the combined approach is the following. The integral equation (19) is determined as a sum:

$$T(x,t) = T_1(x,t) + T_2(x,t) \tag{20}$$

where $T_1(x, t)$ is some arbitrary function of x and t, and $T_2(x, t)$ is composed of a full system of functions of x. It is often convenient to represent T and T_2 in a polynomial form:

$$T_1(x, t) = \sum_{n=0}^{N} a_n(t)x^n \; ; \quad T_2(x, t) = \sum_{n=0}^{N} b_n(t)x^{nr} \; ; \quad r \neq 0$$

Further, by substituting T into the boundary conditions and initial equation (19), all unknown coefficients a_n are determined. When solving the heat conduction equation, the integral method is used in that form in which it is used for large t. Thus, T_1 proves to be integral equation (19) averaged over the existence region under prescribed boundary conditions. By substituting T_2 into the uniform boundary conditions, some of the coefficients b_n are expressed through the others. If the number of boundary conditions is equal to K, the number of independent functions $b_n(t)$ will be equal to $N - K + 1$. Take the first $N - K + 1$ of the coefficients b_n as independent. Then Eq. (20) will be

$$T(x, t) = \sum_{i=0}^{N-K} b_i(t)\chi_i(x, t) + \psi(x, t)$$

The functions $\chi_i(x, t)$ can be regarded here as basic, and consequently the system of variant equations can be made up according to the Kantorovitch method for determining b_i $(i = 0, \ldots N - K)$. It should be noted that the number of coefficients a_n in T_1 is limited by the number of boundary conditions, i.e. a unit more than K. The quantity $b_n \neq 0$ depends both on the number of boundary conditions and on the fact of what approximation is regarded. It is not necessary that the corresponding series should begin with the zero degree as regards x.

By means of the method mentioned above, a solution to any degree of approximation to the accurate one can be obtained. It should be remembered, however, that when solving non-linear problems, one can meet with the necessity to consider a system of non-linear, ordinary differential and algebraic equations. This often causes great difficulties, and naturally leads to limited practical application. Hence, in a number of cases, it is reasonable to use another variant of the combined method, which does not require solving the system of non-linear equations, at least at the stage of specification of initial approach [12].

Key equation and the "ignition" criteria

The mathematical methods discussed above make it possible to do any analytical calculations. In a number of cases, however, this procedure is rather difficult and final results are cumbersome. The problem is simplified by using computers, but the computer method of solution has its disadvantages. Accordingly, it is very important to make the calculation technique easier for the common model, because this makes the latter more available for analysis by simple means. For this purpose two concepts are introduced – the key equation and the "ignition" criteria.

Reduce Eq. (12) to (21):

$$[C_0 + A_c(T - T_0)]\frac{\partial T}{\partial t} = G(T, x, t) + F(T, x, t);$$

$$G(T, x, t) = \frac{\partial}{\partial x}\left\{[\lambda_0 + A_\lambda(T - T_0)]\frac{\partial T}{\partial x}\right\} + \frac{k}{x}[\lambda_0 + A_\lambda(T - T_0)]\frac{\partial T}{\partial x};$$

$$F(T, x, t) = \frac{\partial}{\partial x}\left[\frac{B_\lambda + D_\lambda T^{s+1}}{T^s}\exp\left(-\frac{\phi}{RT}\right)\frac{\partial T}{\partial x}\right] + \frac{k}{x}\,\frac{B_\lambda + D_\lambda T^{s+1}}{T^s}\cdot \tag{21}$$

$$\cdot\exp\left(-\frac{\phi}{RT}\right)\frac{\partial T}{\partial x} - \frac{B_c + D_c T^{s+1}}{T^s}\exp\left(-\frac{\phi}{RT}\right)\frac{\partial T}{\partial t} \pm \Delta H\frac{\partial \alpha}{\partial t}$$

At small conversion degrees the structure of Eq. (21) for reversible and irreversible process will be determined by the character of the operator $G(T, x, t)$. Thus, at the initial stage of transformation and in a dilute sample at any moment of time, the behaviour of the temperature in the cell will be the same for any process. We shall name this equation the key equation. Two facts make it especially valuable. Firstly, its solution determines the behaviour of the base-line. Secondly, (together with the "ignition" criteria introduced below) it permits one to find some kinetic parameters of the process, without solving the entire equation system of the non-linear model.

The complete solution of the key equation is given in [16, 21] for the cells of three classical forms: slab, cylinder, sphere.

Another factor which promotes simplification of calculations connected with the non-linear model is the introduction of the concept of the "ignition" criteria [17, 18]. This term was proposed for the first time in the work [19] considering combustion processes. However, the idea of the approach is due to Zeldovitch [20].

According to the criterion, physico-chemical conversion taking place in the course of warming-up begins to be displayed only from the moment when the thermal energy evolved or absorbed becomes equal to the thermal energy of the external sources, q_{ex}. Determining the temperature T_z from the experimental data (or the time moment) corresponding to the equality of the heat flows, and substituting it into the equation of heat balance,

$$\Delta HZ\int_0^\Delta\left[\exp\left(-\frac{E}{RT_z(x)}\right) - \exp\left(-\frac{E}{RT_0}\right)\right]x^k\,\mathrm{d}x = q_{ex}(T_z) \tag{22}$$

can be determined by varying the scanning speed, activation energy and various complexes including thermophysical parameters. It is characteristic that in order to use the "ignition" criteria, the thermal conduction equation should be solved ignoring the transformation process. In other words, the system of three equations is reduced to one. If λ and C do not depend on T, the thermal conduction equation and boundary conditions are linear and, consequently, are easily integrated.

Denote the thermal energy evolved or absorbed in the conversion process as q_r, and those of all sources in the reference cell and sample cell, respectively, as q_1 and q_2.

In differential scanning calorimetry it is useless to speak about the comparability of heat flows from the external sources and the flow accompanying the transformation processes in a single cell, because, as a rule, $q_r \ll q_1$. However, if the DSC curve is considered to correspond to the temperature of some third hypothetical medium heated by a heat flow $q_2 - q_1$, the application of the "ignition" criteria is quite justified. In this case, the value q_{ex} should be substituted into Eq. (22):

$$q_{ex}(T_z) = \|\, q_2(T_z) \,| - |\, q_1(T_z) \,\|$$

For the fixed sample point the "ignition" criterion will have the following form:

$$\Delta HZ \left\{ \exp\left(-\frac{\gamma E}{RT_z}\right) - \exp\left(-\frac{\gamma E}{RT_0}\right) \right\} = \Big|\, |q_2^{sp}(T_z)| - |q_1^{sp}(T_z)| \,\Big| \tag{23}$$

where $q_1^{sp}(T_z)$ and $q_2^{sp}(T_z)$ are the specific thermal energies at the moment when $T_1 = T_2 = T_z$, and which should be fed into the sample and reference cell, respectively, in order that $T_1(t) \equiv T_2(t)$ at the thermocouple locations.

The expression for the activation energy is easy to obtain from (23):

$$E = \gamma^{-1} \left| \frac{RT_{z_1} T_{z_3}}{T_{z_3} - T_{z_1}} \right| \ln \left| \frac{(\Phi_3 - \Phi_1)\, T_{z_1}(T_{z_2} - T_{z_3})}{(\Phi_3 - \Phi_2)\, T_{z_2}(T_{z_3} - T_{z_1})} \right| ,$$

To summarize the above, it may be said that the "ignition" criteria enable us:

1. In the case when the thermophysical parameters do not depend on temperature, to replace the analysis of a three non-linear equation system of the DSC model by the integration of one linear equation, the exact solution of which is known. This is just the typical situation when the "ignition" criteria may be an express method of evaluating the activation energy in a quick and simple way.

2. In the case when the parameters depend on temperature, to reduce the system of three non-linear equations, the solution of which is very difficult, to one non-linear equation without a source, the approximate integration of which presents no difficulties.

Interpretation of microcalorimetric curve of ADSC

To illustrate the possibilities of the non-linear model and the suggested mathematical apparatus, we shall dwell upon the problem of interpretation of a microcalorimetric curve of an adiabatic differential scanning calorimeter (ADSC). For the sake of simplicity we shall analyze the part which precedes the transformation process. According to the authors' terminology [11], this part corresponds to the predenaturation stage. Further, we shall assume the dependence of the thermophysical parameters upon the temperature to be linear. This approximation is sufficiently good, for example, for water. Actually, the volumetric heat capacity is strictly linear up to the boiling temperature, and the thermal conductivity has only a slight curvature at $T \simeq 70°$.

The detailed solution of the problem is given in [21]. The analytical expression for the recorded energy given by the authors is as follows:

$$\begin{aligned} Q = {} & \frac{2(\lambda_{11} - \lambda_{12})}{(k+1)(1+\gamma)}\Theta + \frac{(k+3)(1+\xi)}{(k+1)(1+\gamma)Q_0}\Bigg[\frac{2(\lambda_{11} - \lambda_{12}}{(k+1)(1+\gamma)} + \\ & + \frac{2Q_0}{1+\xi}(C_{12} - C_{11})\Bigg]\Theta^2 + \frac{4(k+3)(1+\xi)^2}{(k+1)^2(1+\gamma)^2Q_0^2}\Bigg\{\frac{2(\lambda_{11} - \lambda_{12})}{(k+1)(1+\gamma)} + \\ & + \frac{2Q_0}{1+\xi}(C_{12} - C_{11}) + \frac{4(k+1)}{(k+3)(1+\xi)^2(1+\gamma)^2}\big[(C_{11} - C_{12})(C_{11} - \\ & - \lambda_{11} - \gamma\lambda_{12}) - C_{12}^2\gamma\big]\Bigg\}\Theta^3\left[\frac{1}{3!} + \frac{4(k+3)(1+\xi)}{4!(k+1)(1+\gamma)Q_0}\Theta + \ldots\right]; \\ & \xi = \frac{C_{01}}{C_{02}}; \qquad \gamma = \frac{\lambda_{01}}{\lambda_{02}} \end{aligned} \tag{24}$$

Here Q, Θ, C_{1j} and λ_{1j} are dimensionless power, temperature and variables of volumetric heat capacity and thermal conductions of the reference ($j = 1$) and the sample ($j = 2$) cells, respectively [21].

From (24) it follows that the dynamic component of the sample heat capacity is only a constituent of the non-linear part of the general dependence of Q upon the temperature. The linear part of the curve is characterized exclusively by the thermal conductivity of both the reference and the sample. It is quite evident that, depending upon the correlation between the dynamic components λ and C, the behaviour of the calorimetric curve may have the form of either an increasing or a decreasing Θ function, with formation of a plateau or without saturation.

On the basis of the results obtained, we shall analyze the experimental data of the work [22] for dilute solutions of cyanomet-myoglobon MbCN. Since the volumetric heat capacity of MbCN in aqueous solution at $T = 20°$ is $0.55 \cdot \frac{\text{cal}}{\text{g.deg}}$, the following inequality should be fulfilled:

$$\lambda_{11} - \lambda_{12} < 0$$

The latter means that the calorimetric curve will have a saturation region, as it follows from the experiment only at $C_{12} < 0$ and $|C_{12}| < |C_{11}|$. In other words the volumetric heat capacity of cyanomet-myoglobin increases with temperature rise, the temperature coefficient being higher than that of water heat capacity.

In [21] it is shown that for Q at the transition temperature into the saturation region Θ_{sat} the equation is as follows:

$$Q = Q_0\, \Theta_{sat}(C_{11} - C_{12})$$

or passing to dimensional values:

$$\frac{C_{\sim 1}}{C_{01}} - \frac{C_{\sim 2}}{C_{02}} = \frac{Q\alpha C_{02} C_{0MbCN}}{(T_{sat} - T_0)\, Q_{in} C_{01}} \tag{25}$$

Here α is the concentration of MbCN in solution, and C_{0MbCN} C_{01} and C_{02} are the volumetric heat capacity of protein, solvent and solution, respectively, at $T = 20°$.

$$Q_{in} = \frac{Q_0 \alpha C_{MbCN}}{C_{01}}$$

Assuming, for example, that the plateau region for a solution concentration of 1.36% and pH = 9 is reached at $T_{sat} \simeq 63°$, according to (25) we shall have a component in the mixture provided that the heat capacities are additive.

$$C^{sp}_{\sim MbCN} \simeq 10^{-2} \frac{\text{cal}}{\text{g}\cdot\text{deg}^2}$$

It is to be noted that the obtained value of the temperature coefficient of the partial cyanomet-myoglobin heat capacity is the upper boundary of the real value. This is caused by the fact that, due to superposition of the denaturation process and smooth transition into the saturation region, the temperature value T_{sat} does not seem possible to be exactly established. Taking this into account, we have only to state that $C^{sp}_{\sim MbCN}$ is in the range

$$3 \cdot 10^{-4} \frac{\text{cal}}{\text{g.deg}^2} < C^{sp}_{\sim MbCN} < 10^{-2} \frac{\text{cal}}{\text{g.deg}^2}$$

Figure 10 presents an example of a microcalorimetric recording for cyanomet-myoglobin solution. The dot-dash line means a variable constituent of the protein

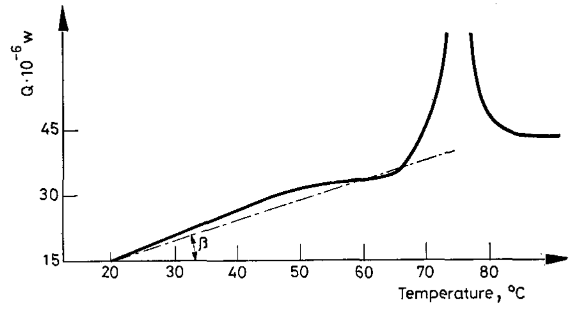

Fig. 10. Microcalorimetric record of the MbCN thermal denaturation at pH 9 and 1.36% of concentration

heat capacity with the assumption that $T_{sat} = 63°$. From Fig. 10 it follows that while using a simplified interpretation the linear part proves to have a temperature coefficient value increased as high as 30%. In fact the error might be much larger, since the real straight line of the partial heat capacity dependence of MbCN upon T may be less steep in the β sector.

An important consequence comes from the fact that the plateau is the property of the linear dependence of C upon T. The specific heat capacity shift ΔC_p at the temperature of conformation transition changes with both the pH change and the denaturation temperature change.

In conclusion, it should be noted that the analytical expression obtained for device-recorded microcalorimetric energy can also be used for the determination of the effective thermal conductivity of a sample.

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RÉSUMÉ — L'article discute les problèmes concernant la théorie de l'analyse calorimétrique différentielle (DSC) non linéaire, en rapport avec le fait que les paramètres thermophysiques dépendent de la température. On montre que les variations de forme de la courbe enregistrée par l'instrument résultent d'un saut de conductibilité thermique et d'un changement de chaleur spécifique lors de la transformation. On donne un modèle correct de DSC non linéaire. On propose un traitement mathématique et quelques notions simplificatrices pour le calcul du modèle non linéaire. On donne comme exemple l'interprétation d'une courbe calorimétrique fournie par un analyseur microcalorimétrique adiabatique, dans le domaine de température précédant la transition.

ZUSAMMENFASSUNG — Der Beitrag erörtert das Problem der nicht-linearen DSC-Theorie im Zusammenhang mit der Abhängigkeit der thermophysikalischen Parameter von der Temperatur. Die Änderungen der durch das Gerät registrierten Form der Wärme-Kraft-Kurve rühren, wie gezeigt wird, von einer jähen Änderung der Wärmeleitfähigkeit her und Änderungen der Wärmekapazität spielen im Laufe des Prozesses ebenfalls mit. Ein korrektes nicht-lineares DSC-Modell wird formuliert. Der mathematische Apparat und einige vereinfachende Begriffe zur Errechnung des nicht-linearen Modells werden vorgeschlagen. Als Beispiel wird die Interpretation einer kalorimetrischen Kurve eines adiabatischen Scanning-Mikrokalorimeters gegeben, das den Vor-Übergangs-Bereich von Temperaturen erfaßt.

Резюме — В настоящей работе рассматриваются вопросы нелинейной теории ДСК, связанные с зависимостью теплофизических параметров от температуры. Показывается к каким изменениям в форме регистрируемой прибором тепловой мощности приводит учёт скачка теплопроводности и сдвига теплоёмкости в ходе превращения. Формулируется строгая нелинейная модель ДСК. Предлагается математический аппарат и некоторые упрощающие понятия для расчётов по нелинейной модели. В качестве примера рассматривается вопрос об интерпретации калориметрической кривой адиабатического дифференциального сканирующего микрокалориметра в предпереходной области температур.