Heat Transfer and Phase Transition in DTA Experiments

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Chapter 5

Heat transfer and phase transition in DTA experiment

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5.1 Historical outline of methods studying thermal behavior

Early principles of *thermometry* [1–3] were already established by *Galileo Galilei* (1564–1642) whose idea was to make use of the volume changes of gases while observing the alongside changes in thermal state of given bodies (air thermometer). The first liquid thermometer was likely constructed by *J. Rey* in 1631 and the description of mercury thermometer is ascribed to *Daniel G. Fahrenheit* in 1724. The elaboration of the earliest ice calorimeter is credited to *A. L. Lavoisier* and *Pierre S. Laplace* around 1790 [4, 5] coining the term from the Latin "calor" and the Greek "meter". Sourced on the work by *B. Telesio* (1509–1588) [6], *Jan A. Comenius* (1592–1670) [7] made use of the term "caloric" when describing the importance of concepts of cold and warm [1].

A novel method of combustion calorimeter emerged in Copenhagen [8–10] and consequent setup of Bunsen calorimetry [11] was based on the replacement of measurement of the mass of melted ice with that designed to volume changes (i.e. ware phase transition modified by *Wojciech Swietoslawski* (1881–1968) [12]). Further achievement was the introduction of low temperature calorimetry in 1892 upon the development of a vacuum vessel by *James Dewar* (1842–1923) first determining specific heats of metals at low temperatures. In the turn of twenties *Albert Tian* (1881–1974) and *Eduard Calvet* (1895–1966) started methodical investigation aimed at the application of the Peltier and Joule effects to the compensation of heat generated during calorimetric studies. Categorization of calorimeters according to the temperature difference between the sample-block T_B and surrounding jacket T_J was suggested by *Velíšek* [15, 16].

Modern thermometry introduced the term thermal analysis dated back to the 18th century when the temperature became better understood as an observable and experimentally monitorable quantity. First note came from Uppsala in 1829 where *Friedrik Rudberg* (1800–1839) recorded inverse cooling-rate data for lead, tin, zinc and various alloys. The bare equipment consisted of an iron crucible suspended by thin platinum wire at the center of a large double-walled iron vessel provided with a tight-fitting, dished with iron lid, through which passed a thermometer with its bulb in the sample. The inner surface of the outer container and the outer surface of the crucible were blackened to permit the maximum achievement of heat transfer. The spaces between two walls of the outer large vessel, as well as the top lid, were filled with snow to ensure that the inner walls were always kept at zero temperature. In this way a controlled temperature program was ensured once the crucible with molten metal or alloy had been positioned inside and the lid closed. Once the experiment was set up Rudberg noted and tabulated the times taken by the mercury in thermometer to fall through each 10 degrees interval. The longest interval then included the freezing point.

The next experiment that falls into the category of thermal analysis was done in 1837 by *Frankenheim* who described a method of determining cooling curves (temperature *vs.* time). This method was later associated with the so-called *Hannay's* time method, when temperature is increased continuously (such a plot would resemble what we now call 'isothermal mass-change curves'). In 1883, *Henry L. Le Chatelier* (1850–1936) adopted a somehow more fruitful approach immersing the bulb of thermometer within the sample in an oil bath, which

maintained a constant temperature difference (usually 20° between the thermometer and another one placed in the bath). He plotted the time vs. temperature curve easily convertible to the sample vs. environmental temperatures, factually introducing the 'constant-rate' or 'quasi-isothermal' program.

The development of thermocouple, as an accurate temperature measuring device, was rapidly followed by *Floris Osmond* (1849–1912) who in 1886 investigated the heating and cooling behavior of iron and steel with a view to elucidate the effects of carbon so that he factually introduced thermal analysis into the most important field: metallurgy. However, in 1891, *William C. Roberts-Austen* (1843–1902) [18] was known to construct a device to give a continuous record of the output from thermocouple and he termed it as 'Thermoelectric Pyrometer'.

Though the sample holder was a design reminiscent of modern equipment, its capacity was extremely large decreasing thus the sensitivity but giving a rather good measure for reproducibility. It was quickly realized that a galvanometer was rather insensitive to pick up small thermal effects. This disadvantage was improved by coupling two galvanometers in parallel and later the reflected light beam was directed to the light-tight (dark) box together with the slit system enabling exposition of the repositioned photographic plate. In 1899 *Stanfield* published heating curves for gold and almost stumbled upon the idea of DTA (*Differential Thermal Analysis*) when maintaining the 'cold' junction at a constant elevated temperature measuring thus the differences between two high temperatures. Roberts-Austen consequently devised the system of measuring the temperature difference between the sample and a suitable reference material placed side-by-side in the same thermal environment, thus initiating development of DTA instruments. Among other well-known inventors, Russian *Nikolay S. Kurnakov* (1860–1941) [19] should be noticed as he improved registration, building his pyrometer on the photographic, continuously recording drum, which, however, restricted his recording time to mere 10 minutes.

The entire term *thermal analysis* was finally coined by *Gustav Tammann* (1861–1938) [20] around 1904 who demonstrated theoretically the value of cooling curves in phase-equilibrium studies of binary systems. By 1908, the heating or cooling curves, along with their rate derivatives and inverse curves, acquired enough sufficient importance to warrant a first review and a more detailed theoretical inspection was given by George K. Burgess (1874–1932) [21]. Not less important was the development of heat sources where coal and gas were almost completely replaced by electricity as the only source of controllable heat. In 1895, *Georges A. A. Charpy* (1865–1945) described in detail the construction of wire-wound, electrical resistance, tube furnaces that virtually revolutionized heating and temperature control. Indeed the heating rate control had to be active to avoid possibility of irregularities; however, little attention was paid to it as long as the heat source delivered a smooth temperature-time curve. All early users mention temperature control by altering the current and many descriptions indicate that this was done by manual or clockwork-based operation of a rheostat in series with the furnace winding, the system in practical use up to late fifties.

The first automatic control was introduced by *K. Friedrich* in 1912 using a resistance box with a specially shaped, clock-driven stepped cam on top. As the cam rotated it displaced a pawl outwards at each step and this in turn caused the brush to move on to the next contact, thus reducing the resistance of furnace winding. Suitable choice of resistance and profiling of the cam achieved the desired heating profile. The sample size was also reduced from 25 g down to 2.5 g, to decrease the uncertainty in melting point determination from about 2 K to 0.5 K. Rates of about 20 K/min were fairly common during the early period later decreased to about quarter. It was *G. K. Burgess* [21] who considered meaning of various curves in detail and concluded that the area of the inverse-rate curve is proportional to the quantity of heat generated divided by the rate of cooling.

Only few papers published in the period up to 1920 gave little experimental details so that *W. P. White* [22] was first to show theoretically in 1909 the desirability of smaller samples describing more exhaustively the effect of experimental variables on the shape of heating curves as well as the influence of temperature gradients and heat fluxes taking place within both the furnace and the sample. It is obvious that DTA was initially more an empirical technique, although the experimentalists were generally aware of its quantitative potentialities going back to historic times of *Isaac Newton* (1642–1727) [23] who published his temperature scale in 1701, the significance of which lies both in its range of temperature and in its instrumentation presenting also the famous Newton's Law of Cooling. However, the foremost milestone in the theory of heat propagation was provided by *Jean B. J. Fourier* (1768–1830) [24] who initiated the investigation of Fourier series and their application to problems of heat transfer. The early quantitative studies were treated semi-empirically and based more on instinctive reasoning. In 1939 *F. H. Norton* published his classical paper [25] on techniques where he made rather excessive claims for its value both in the identification and quantitative analysis exemplifying clay mixtures. The

first more detailed theories, absent from restrictions, became accessible in a series of papers [25–32] and later books [33–40], historical roots are shown in [1, 2, 41–46].

Recently, the commercial DTA instruments are often classified as a *double non-stationary calorimeter* [41–44] in which the thermal behaviour of the sample is compared with a correspondingly mounted, inert reference. It implies control of heat flux from surroundings and heat itself is understood to be a kind of physical-chemical reagent, which, however, could not be directly measured but calculated on the basis of the measurable temperature gradients. It should be noted that heat flow mediated by mass-less phonons so that the inherent flux does not exhibit inertia, as is the case for the flow of electrons. The thermal inertia of apparatus (as observed in DTA experiments) is thus caused by heating a real body and is affected by the real properties of materials forming the sample under study. The quandary of thermal inertia term in the DTA equation was first noticed by *M. M. Faktor*, *R. Hanks* [47] and detailed in consequent work of *A. P. Grey* [48] and *P. Holba* and *J. Šesták* [49, 50] and is the subject of our further analysis.

5.2 DTA equation and its testing by rectangular heat pulse

Starting from the analysis of the heat transfer process under the conditions of DTA apparatus and using ideas of Faktor & Hanks [47] the simple balances of heat fluxes for sample and reference holders were found [49, 50]:

Sample holder: $K_S\left(T_W - T_S\right) = C_P^S\left(dT_S/dt\right) - \Delta_t H\left(d\xi/dt\right)$ (5.1)

Reference holder: $K_R\left(T_W - T_R\right) = C_P^R\left(dT_R/dt\right)$ (5.2)

where K_S, K_R are the coefficients of heat transfer between the furnace wall (with temperature T_W) on one side and the sample holder (with temperature T_S) and the reference holder (with temperature T_R) on the other side, respectively; C_P^S and C_P^R are the heat capacities of sample holder (including sample) and reference holder (including reference material); $\Delta_t H$ is the enthalpy change of phase transition (positive for endothermic process) and $d\xi/dt$ is the rate of the transition (ξ is the progress variable or extent of transition and t means time).

From the balances, the DTA equation (expressing temperature difference ΔT_{DTA} between the sample and the reference holders) was derived in the form:

$$\Delta T_{DTA} = \frac{1}{K_{DTA}}\left(\Delta K(T_W - T_R) - (C_P^S - C_P^R)\Phi - C_P^S \frac{d\Delta T}{dt} + \Delta_t H \frac{d\xi}{dt}\right)   (5.3)$$

where $\Delta T_{DTA} = T_S - T_R$; $\Delta K = K_S - K_R$; $\Phi = dT_R/dt$ (linear heating rate); $K_{DTA} = K_R$ („apparatus constant" of DTA depending on temperature T_R and heating rate Φ).

The heat capacity of sample C_P^S can be expressed as depending on the extent of transition ξ

$$C_P^S = C_{P\,in}^S + \xi\,\Delta_t C_P^S   (5.4)$$

where $C_{P\,in}^S$ is the initial heat capacity of sample (including sample holder) and $\Delta_t C_P^S$ is the heat capacity change due to transition, for which Person–Kirchhoff equation is valid:

$$\Delta_t C_P^S = \left(\frac{\partial \Delta_t H}{\partial T}\right)_P   (5.5)$$

4
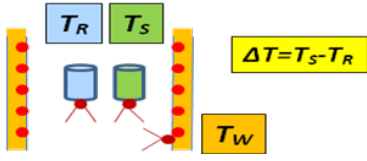
Fig. 5.1 Arrangement of the sample (S) and reference (R) holders with respect to the furnace wall.
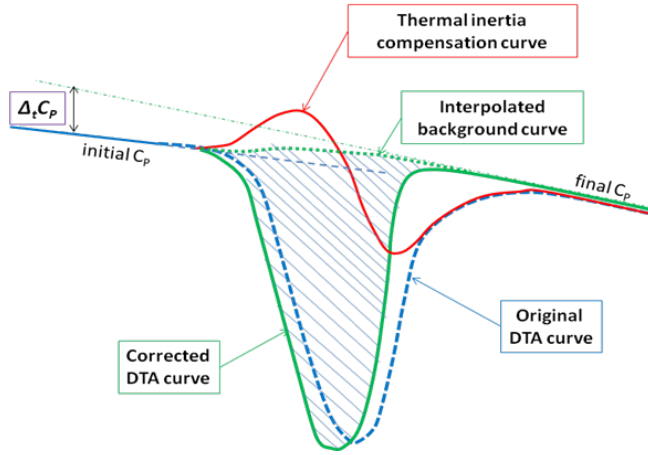
Fig. 5.2 Correction of DTA curve with respect to thermal inertia

Such a rather important expediency of the heat inertia appearance in the frame of DTA equation remained overlooked in most, even recent books [53], with few exceptions [16, 43, 44] so it has been a remaining question if it is mere theoretical fiction or a real experimental output. Therefore, an artificial exothermic process was experimentally initiated by introducing a rectangular heat pulse inside sample holder of DTA apparatus [52] and the equation of heat flux balances (DTA equation) was used to desmeare the resulting DTA curve and to reconstruct the applied heat pulse.

The result of the mentioned procedure is shown in Fig. 5.4. Correction made using the DTA equation gives the desmeared curve more similar to the original pulse, but the differences remain near the onset and the end of the heat pulse. Therefore, the question arose what is the cause of this insufficiency.
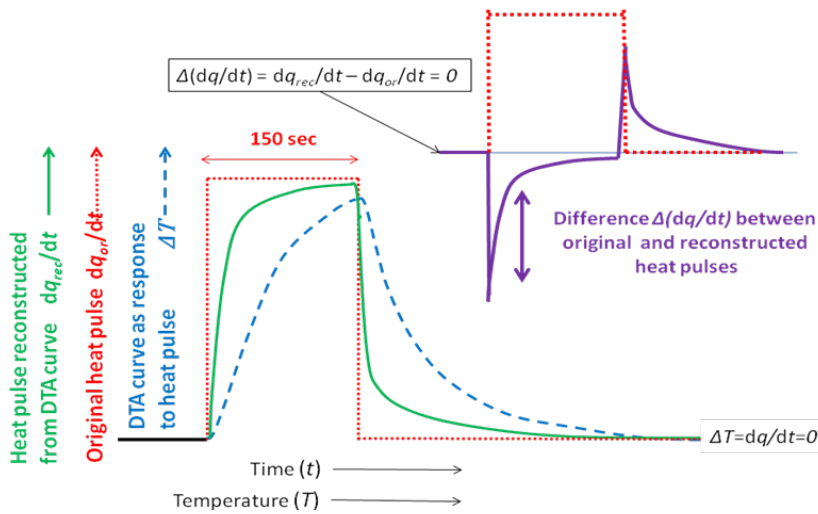

Fig. 5.3 Use of DTA equation (5.3) for reconstructing the heat pulse from DTA curve as a response to artificial rectangular heat pulse [52]. The greatest differences between the original and reconstructed heat process is in the fields near to the onset and the end of rectangular pulse, where the heat flux is abruptly changed ($\ddot{q} \equiv \mathrm{d}^2q/\mathrm{d}t^2 \to \pm\infty$).

The most probable origin of the incomplete desmearing seems to be a simplification used in the formulation of heat flux balances, where only single temperatures (T_S and T_R) are used to characterize the whole sample and the whole reference. In fact, the temperature of any material body exposed to heating (or cooling) even if the material is thermally inert (not exhibiting any heat consuming or heat generating process – reaction or transition) is not uniform so that the „termoscopic state" of the body should be described by a temperature field $T(x, y, z)$ – by a dependence of an instantaneous local temperature T on space coordinates x, y, z. The estimation of this „nonuniformity of temperature" and its impact on the shape of DTA curve represents the main objective of this chapter.

5.3 Temperature fields inside an inert material in a form of infinite cylinder

The simplest way to analyze the influence of nonuniform temperature field on the shape of DTA curve is to start from the simplifying assumption that both the sample and the reference have a form of infinite cylinder with the same radius r_E. Then the local temperature T can be represented as a function of only one dimension – local radius r. Consider two cylinders of infinite length denoted as R (reference) and S (sample) centered on the axes of two identical vertical tube furnaces. Internal cylindric walls of both furnaces have at any moment the same temperature T_W which guarantees a linear increase of temperature T_{RE} detected at surface of cylinder formed by reference material corresponding to a constant heating rate $\Phi_{RE} = dT_{RE}/dt$. At the surface of the sample, the temperature T_{SE} is detected and the difference $\Delta T = T_{SE} - T_{RE}$ is then an output signal recorded as the DTA curve.

Such conditions make it possible to represent the temperature fields by one-dimensional functions $T_R(r)$ for the reference and $T_S(r)$ for the reference and the sample, respectively, as shown in Fig. 5.5.
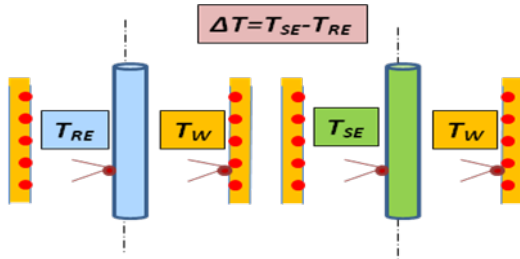
Fig. 5.4 Arrangement of an idealized DTA experiment with infinitely long cylinders formed from reference material (with surface temperature T_{RE}) and from sample (with T_{SE}) exposed to heated furnace walls (with the same temperature T_W)

At the idealized conditions mentioned above, no heat transfer between the sample and the reference exists and the apparatus constant K_{DTA} should have the same value for the sample as for the reference. However, the parameter K_{DTA} depends in general on temperature, particularly at higher temperatures where the heat transfer by radiation takes place. If we consider a heat flux $\dot{q}_{SE}$ (in W/m) between the furnace wall (with temperature T_W) and the external surface of the sample (with temperature T_{SE}) related to a unit length of an infinite cylinder with the radius r_E as consisting of two parts: the conductive $\dot{q}_{cond}$ and the radiation $\dot{q}_{rad}$ fluxes

$$\dot{q}_{SE} = K_{DTA}\left(T_W - T_{SE}\right) = \dot{q}_{cond} + \dot{q}_{rad}$$
$$= 2\pi r_E \left[\lambda_{atm}\left(T_W - T_{SE}\right) + \sigma \, \Im_W \left(T_W^4 - T_{SE}^4\right)\right] \tag{5.6}$$

where λ_{atm} is the thermal conductivity (in W/m/K) of atmosphere between the furnace wall and the sample, σ is the Stefan–Boltzmann constant ($\sigma = 5.67 \times 10^{-8}$ W m^{-1} K^{-4}) and $\Im_W$ is a dimensionless factor reflecting the shape and emitivity character of the system furnace-sample, then the apparent heat transfer coefficient K_{DTA} – „apparatus constant" (in W/K) – is found as the third-order polynomial function of temperature T_{SE}

$$K_{\text{DTA}}\left(T_{\text{SE}}\right) = 2\pi r_{\text{E}}\left[\lambda_{\text{atm}} + \sigma\, \Im_{\text{W}}\left(T_{\text{W}} + T_{\text{SE}}\right)\left(T_{\text{W}}^2 + T_{\text{SE}}^2\right)\right] \qquad (5.7)$$

where the decomposition $(a^4 - b^4) = (a^2 - b^2)(a^2 + b^2) = (a - b)(a + b)(a^2 + b^2)$ is used.

If an equation analogous to (5.7) is used for the temperature at the reference surface T_{RE}, then the difference ΔK_{DTA} is estimated by approximation using the first term of Taylor series:

$$\Delta K_{\text{DTA}} = K_{\text{DTA}}\left(T_{\text{SE}}\right) - K_{\text{DTA}}\left(T_{\text{RE}}\right) \approx \frac{dK_{\text{DTA}}}{dT}\Delta T_{\text{DTA}}$$

$$\approx 2\pi r_{\text{E}}\left[\frac{d\lambda_{\text{atm}}}{dT} + \sigma\, \Im_{\text{W}}\left(T_{\text{W}}^2 + 2T_{\text{W}}T_{\text{SE}} + 3T_{\text{SE}}^2\right)\right]\Delta T_{\text{DTA}} \qquad (5.8).$$

The afore-mentioned dependence of apparatus constant K_{DTA} on temperature (T_{SE}) as well as on temperature difference ΔT_{DTA} will be neglected in the following considerations focused on the effect of temperature field nonuniformity on the shape of DTA curves.

5.3.1 Stabilized temperature profile in homogeneous substance at linear heating

Consider a reference material which does not exhibit any reaction or transition within the temperatures region under study and assume its molar heat capacity $C_{P,\text{m}}^{\text{R}}$ (or specific heat capacity c_{R} related to unit mass), molar volume V_{m}^{R} (or density ρ_{R} and molar mass M_{R}) and heat conductivity λ_{R} are independent on temperature T. The heat capacity of the reference C_{R} related to unit volume is then given by

$$C_{\text{R}} = \frac{C_{P,\text{m}}^{\text{R}}}{V_{\text{m}}^{\text{R}}} = c_{\text{R}}\rho_{\text{R}} = \frac{C_{P,\text{m}}^{\text{R}}\rho_{\text{R}}}{M_{\text{R}}} \qquad \text{in } J/(K\,m^3) \qquad (5.9)$$

and the thermal diffusivity α_{R} is given as

$$\alpha_{\text{R}} = \frac{\lambda_{\text{R}}}{C_{\text{R}}} \qquad \text{in } m^2/s \qquad (5.10)$$

It follows from the Fourier equation that the heat flux $\dot{q}_{\text{RE}}$ entering the reference cylinder is proportional to the temperature gradient at the surface $g_{\text{RE}} = (dT_{\text{R}}/dr)_{r=r_{\text{E}}}$, where $T_{\text{R}}(r)$ means the temperature field in the reference and r_{E} is the external radius of the cylinder:

$$\dot{q}_{\text{RE}} = 2\pi r_{\text{E}} g_{\text{RE}} \lambda_{\text{R}} \qquad (5.11)$$

If the introducing flux is consumed to heat the reference substance in the whole volume of cylinder:

$$\dot{q}_{\text{RE}} = \int_0^{r_{\text{E}}} 2\pi C_{\text{R}} \frac{dT_{\text{R}}(r)}{dt} r\, dr = 2\pi C_{\text{R}} \int_0^{r_{\text{E}}} \frac{dT_{\text{R}}(r)}{dt} r\, dr \qquad (5.12)$$

it follows for any cylindrical shell of thickness dr at a distance r from the cylinder axis

$$\left(\frac{d^2 T_{\text{R}}(r)}{dr^2} + \frac{1}{r}\frac{dT_{\text{R}}(r)}{dr}\right)\lambda_{\text{R}} = C_{\text{R}}\frac{dT_{\text{R}}(r)}{dt} \qquad (5.13)$$

Using (5.10) the following differential equation is found:

$$\frac{d^2 T_R(r)}{dr^2} + \frac{1}{r}\frac{dT_R(r)}{dr} = \frac{1}{\alpha_R}\frac{dT_R(r)}{dt} \tag{5.14}$$

The actual local temperature T_R inside the reference is a function of time t and the position r (measured as the distance from axis): $T_R(r, t)$. In the case of temperature independent thermal diffusivity α_R, the local temperature $T_R(r, t)$ can be expressed as a sum of time-dependent temperature on the reference surface $T_{RE}(t)$ and of the temperature deviation $\theta_R(r)$ depending only on the distance from axis r

$$T_R(t,r) = T_{RE}(t) + \theta_R(r) \tag{5.15}$$

Then it follows for the field of temperature gradients $g_R(r)$

$$g_R(r) = \frac{dT_R(r)}{dr} = \frac{d\theta_R(r)}{dr} \tag{5.16}$$

and for the local heating rate $dT_R(r)/dt$

$$\frac{dT_R(r)}{dt} = \frac{dT_{RE}}{dt} = \Phi_{RE} = \text{const} \tag{5.17}$$

The differential equation (5.14) is then simplified into

$$\frac{d^2\theta_R(r)}{dr^2} + \frac{1}{r}\frac{d\theta_R(r)}{dr} = \frac{1}{\alpha_R}\Phi_{RE} \tag{5.18}$$

i.e.
$$\frac{dg_R(r)}{dr} + \frac{g_R(r)}{r} = \frac{\Phi_{RE}}{\alpha_R} \tag{5.19}$$

and the following solution is found

$$\theta_R(r) = -\frac{\Phi_{RE}}{4\alpha_R}(r_E^2 - r^2) \tag{5.20}$$

The temperature field in linearly heated reference is then defined by

$$T_R(r) = T_{RE} - \frac{\Phi_{RE}}{4\alpha_{RE}}(r_E^2 - r^2) \tag{5.21}$$

and the field of temperature gradient $g_R(r)$ turns out to be linear in r

$$g_R(r) = \frac{\Phi_{RE}r}{2\alpha_R} \tag{5.22}$$

The temperature field established at linear heating (or cooling) rate given by Eq. (5.21) will be referred as the „stabilized temperature profile".

The stabilized temperature profile corresponding to equation (5.21) is to be expected at any material (substance) under the condition of stabilized linear heating in the temperature range where no reaction or transition can occur.
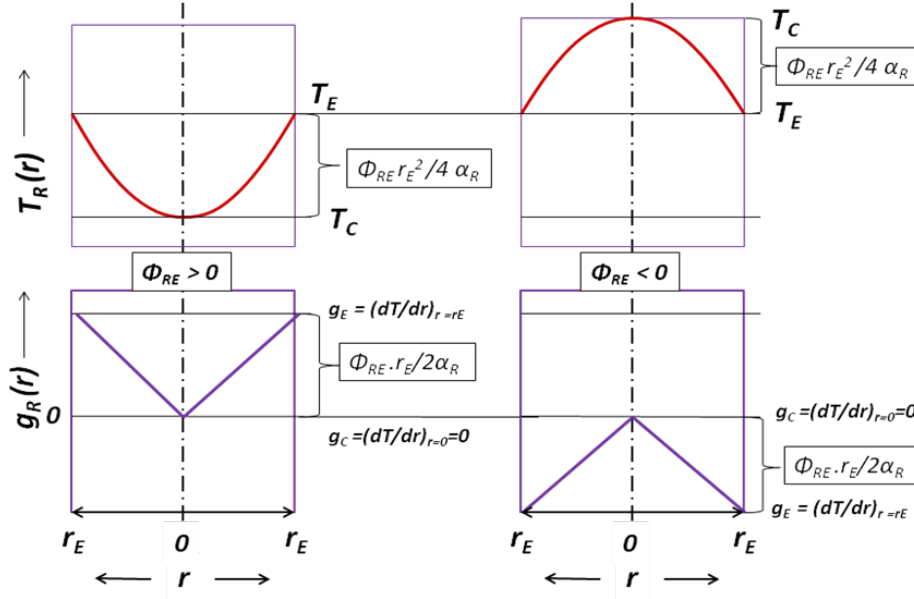
Fig. 5.5 Stabilized temperature profile $T_R(r)$ and gradient profile $g_R(r)$ at linear heating ($\Phi_{RE} > 0$) and linear cooling ($\Phi_{RE} < 0$) in infinite cylinder with external radius r_E.

5.3.2 Stabilized temperature profile in a cylinder composed of core material surrounded by coaxial jacket (holder) material

If a sample material is inserted into an infinitely long cylindrical holder with a thickness δ_H then the external surface exposed to heating has the radius $r_H = r_E + \delta_H$. Consider the holder material has a heat capacity (related to a unit volume) C_H and a heat conductivity λ_H. Heat flux $\dot{q}_{HE}$ coming from outside into the holder (of a unit length) with a surface temperature $T_{HER} = T_H(r_H)$ given as

$$\dot{q}_{HE} = 2\pi r_H \lambda_H g_{HE} \tag{5.23}$$

is partly consumed to increase the local temperature $T_H(r)$ in the range $r_H \geq r \geq r_E$ while the rest of the heat flux $\dot{q}_{RE}$ into the reference:

$$\dot{q}_{HE} = 2\pi \int_{r_E}^{r_H} C_H \frac{dT_H(r)}{dt} r \, dr + \dot{q}_{RE} \tag{5.24}$$

At the interface between the holder and the reference material (at the radius r_E) the heat flux from the holder into the reference $\dot{q}_{HR}$ must be equal to the heat flux $\dot{q}_{RE}$ (given by Eq. 5.11), so that:

$$\dot{q}_{HR} = 2\pi r_E \lambda_H g_{HR} = 2\pi r_E \lambda_R g_{RE} = \dot{q}_{RE} \tag{5.25}$$

It follows that the gradient g_{HR} at the internal surface of the holder is determined by

$$g_{HR} = g_{RE} \frac{\lambda_R}{\lambda_H} \tag{5.26}$$

Assuming a stabilized temperature field at linear heating (or cooling) the local heating rates are uniform and equal to Φ_{RE}:

$$\frac{dT_H(r)}{dt} = \frac{dT_{RE}}{dt} = \Phi_{RE} \qquad (5.27)$$

Neglecting the temperature dependence of C_H and λ_H, the stabilized temperature field $T_H(r)$ can be derived in the following form:

$$T_H(r) = T_{RE} + \frac{\Phi_{RE}}{4\alpha_H}(r^2 - r_E^2) \qquad (5.28)$$

where $\alpha_H = \lambda_H/C_H$ is the thermal diffusivity of the holder material. The temperature at the external surface of the holder T_{HER} is then related to temperature T_{RE} by the following formula

$$T_{HER} = T_{RE} + \frac{\Phi_{RE}}{4\alpha_H}(r_H^2 - r_E^2) \qquad (5.29)$$
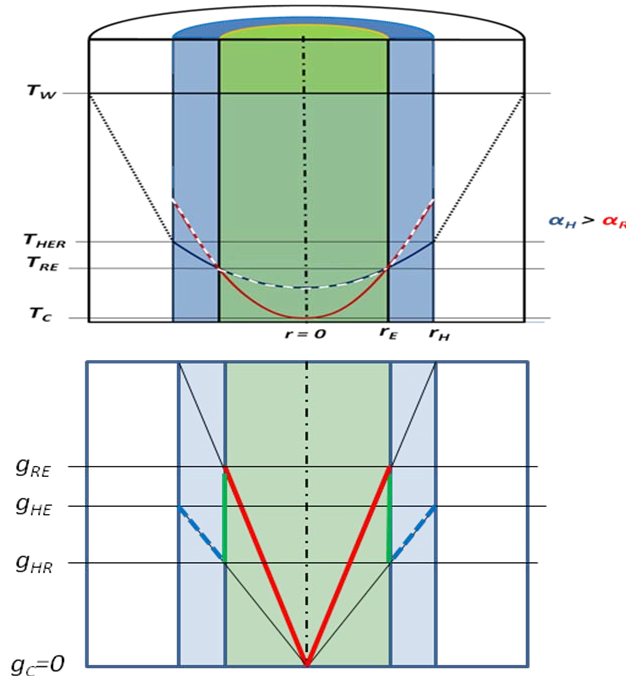
Fig. 5.6 Stabilized temperature profiles $T_R(r)$, $T_H(r)$ and gradient profiles $g_R(r)$, $g_H(r)$ at linear heating ($\Phi_{RE} > 0$) in an infinite cylinder with external radius of holder (jacket) r_H and external radius of reference (core) r_E in the case when the thermal diffusivity of holder material α_H is greater than that of the reference material α_R ($\alpha_H > \alpha_R$).

5.3.3 Temperature profile in a hollow cylinder at stationary (steady) heat flow

Consider a hollow cylinder with an infinite length, internal (inner) radius r_I and outer radius r_E which is made of a material R and it separates two surroundings: the outer with temperature T_E and the inner with temperature T_I. If a stationary (steady) state is reached then the heat flux $\dot{q}_R(r)$ through the cylindrical shell at any distance r from the axis should be the same so that:

$$\dot{q}_R(r) = 2\pi r g_R(r)\lambda_R = \text{const}_{st} \qquad (5.30)$$

where λ_R is the heat conductivity of material R and $g_R(r)$ is the local temperature gradient. It follows from Eq. 5.30 that the local gradient must be proportional to reciprocal of distance r

$$g_R(r) = \frac{dT_R(r)}{dr} = \frac{\text{const}_{st}}{2\pi\lambda_R}\frac{1}{r} \qquad (5.31)$$

which implies the differential equation

$$dT_R(r) = \frac{\text{const}_{st}}{2\pi\lambda_R}\frac{1}{r}dr \qquad (5.32)$$

Assuming λ_R is independent from temperature, the following relation is found

$$T_E = T_I + \frac{\text{const}_{st}}{2\pi\lambda_R}\int_{r_I}^{r_E} d\ln r = T_I + \frac{\text{const}_{st}}{2\pi\lambda_R}\ln\frac{r_E}{r_I} \qquad (5.33)$$

The unknown constant const_{st} is thus determined from Eq. 5.33
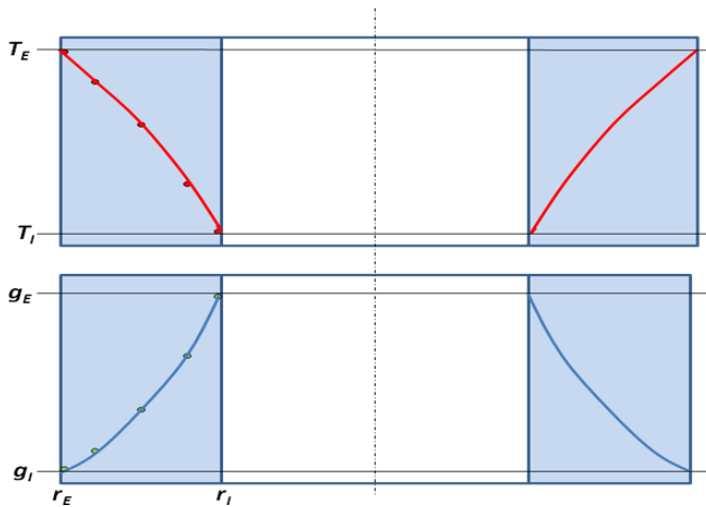
$$\text{const}_{st} = 2\pi\lambda_R\frac{T_E - T_I}{\ln r_E/r_I} \qquad (5.34)$$

and the steady-state temperature profile $T_R(r)$ is derived as

$$T_R(r) = \frac{T_E - T_I}{\ln r_E/r_I}\int_{r_I}^{r} d\ln r + T_I = T_I + (T_E - T_I)\frac{\ln r/r_I}{\ln r_E/r_I} \qquad (5.35)$$

whereas the radial profile of steady-state gradient is determined as

$$g_R(r) = \frac{dT_R(r)}{dr} = \frac{T_E - T_I}{\ln r_E/r_I}\frac{d\ln r}{dr} = \frac{T_E - T_I}{\ln r_E/r_I}\frac{1}{r} \qquad (5.36)$$

Fig. 5.7 Stationary temperature profile $T_R(r)$ and gradient profile $g_R(r)$ in hollow cylinder with outer radius r_E and inner radius r_I separating outer reservoir with temperature T_E and inner reservoir with temperature T_I in case $r_I = r_E/2$ and $T_E > T_I$

5.4 Temperature profile in a sample exhibiting first-order phase transition

Consider a sample in the form of infinite cylinder with external radius r_E. The sample exhibits an endothermic first-order phase transition with the equilibrium transition temperature T_t and molar enthalpy change $\Delta_t H_m$. During the transition, the initial phase φ_i with molar volume V_m^i, molar heat capacity $C_{P,m}^i$ and heat conductivity λ_i is changed into the final phase φ_f with the respective quantities V_m^f, $C_{P,m}^f$ and λ_f. The overall extent of transition ξ_G is determined as fraction of molar amount of the final phase N_f (molar amount of the transformed part of sample) referred to the whole sample:

$$\xi_G = \frac{N_f}{N_i + N_f} \tag{5.37}$$

where N_i is molar amount of the nontransformed part of sample (molar amount of remaining initial phase).

To avoid the problems of changing radius due to molar volume change at the transition, it is assumed that the transition does not change the sample volume: $V_m^i = V_m^f$; $\Delta_t V_m = 0$.

When the sample is exposed to a linear heating then four stages can be distinguished with respect to the temperature profile inside the sample.

I. Temperature at any part of the sample is lower than the (equilibrium) transition temperature $T_t > T$ so that the stabilized temperature profile occurs inside the sample in the form

$$T_i(r) = T_{SE} - \frac{\Phi_{RE}}{4\alpha_i}(r_E^2 - r^2) \tag{5.38}$$

where $\alpha_i = \lambda_i V_m^i / C_{P,m}^i$ represents the thermal diffusivity of the initial phase φ_i, T_{SE} is the temperature detected on the sample surface and $\Phi_{RE} \approx dT_{SE}/dt$ is the applied linear heating rate.

II. Temperature higher than T_t in a part of the sample, the phase transition is in progress and the extent of transition inside the whole is lower than unity ($0 < \xi_G < 1$). The temperature profile is not stabilized since it is affected by a „heat sink" heat due to the running endothermic transition.

III. Temperature at any part of the sample is higher than T_t and the extent of transition is equal to unity; however, the temperature profile is not yet stabilized but it is tending to reach the stabilized state.

IV. The stabilized temperature profile after the transition is reached in the form:

$$T_f(r) = T_{SE} - \frac{\Phi_{RE}}{4\alpha_f}(r_E^2 - r^2) \tag{5.39}$$

where $\alpha_f = \lambda_f V_m^f / C_{P,m}^f$ represents the thermal diffusivity of the final phase φ_f.

The thermal behaviour of the sample upon the transition can be approached using two different models; a continuous and a discontinuous one.

5.4.1 Continuous model of phase transition

For the sample under study in the form of an infinite cylinder with the radius r_E the Fourier law applied to the reference by (5.13) should be modified in order to involve the heat consumed by endothermic transition whose local extent $\xi_r(r)$ and local temperature $T_S(r)$ inside the sample are functions of the radius r:

$$\left(\frac{d^2 T_S(r)}{dr^2}+\frac{1}{r}\frac{dT_S(r)}{dr}\right)\lambda_S = \frac{C^S_{P,m}}{V^S_m}\frac{dT_S(r)}{dt}+\frac{\Delta_t H_m}{V^S_m}\frac{d\xi_r(r)}{dt} \tag{5.40}$$

where $\Delta_t H_m$ stands for the enthalpy change associated with the transition. For the sake of simplicity, the properties of initial φ_i and final φ_f phases are assumed to be equal such that

$$\lambda_S = \lambda_i = \lambda_f \quad C^S_{P,m} = C^i_{P,m} = C^f_{P,m}, \quad V^S_m = V^i_m = V^f_m$$

and hence

$$\alpha_S = \frac{\lambda_S V^S_m}{C^S_{P,m}} = \alpha_i = \alpha_f \tag{5.41}$$

Eq. 5.40 can be thus rewritten into the form

$$\left(\frac{d^2 T_S(r)}{dr^2}+\frac{1}{r}\frac{dT_S(r)}{dr}\right) = \alpha_S\left(\frac{dT_S(r)}{dt}+\frac{\Delta_t H_m}{C^S_{P,m}}\frac{d\xi_r(r)}{dt}\right) \tag{5.42}$$

For the rate of local transition $d\xi_r(r)/dt$ the simplest model could be applied starting from the idea the rate is proportional to „overheating" of a given cylindrical shell, i.e. to the difference between the local temperature and the equilibrium transition temperature: $(T_S(r) - T_t)$ – and to the local fraction of the non-transformed substance (initial phase φ_i): $(1 - \xi_r(r))$

$$\frac{d\xi_r(r)}{dt} = k_\xi\left(T_S(r)-T_t\right)\left(1-\xi_r(r)\right) \tag{5.43}$$

Substituting Eq. (5.43) into Eq. (5.42) we obtain

$$\left(\frac{d^2 T_S(r)}{dr^2}+\frac{1}{r}\frac{dT_S(r)}{dr}\right) = \alpha_S\left(\frac{dT_S(r)}{dt}+R_{hc}k_\xi\left(T_S(r)-T_t\right)\left(1-\xi_r(r)\right)\right) \tag{5.44}$$

where $R_{hc} = \Delta_t H_m/C^S_{P,m}$.

Solving the differential equation (5.44) for the model values $T_t = 800\,°C$, $\Phi = 0.2$ K/s, $\lambda_S = 0.02$ W cm^{-1} K^{-1}, $C^S_{P,m}/V^S_m = 4$ J cm^{-3} K^{-1}, $\Delta_t H_m/V^S_m = 400$ J cm^{-3}, and $K_{DTA} = 1$ W cm^{-1} K^{-1}, using the software for solving partial differential equations [56] the results on T_S profiles, the local extent of transition ξ_r as well as the respective rates have been found as it is shown in Figs. 5.8–5.9.
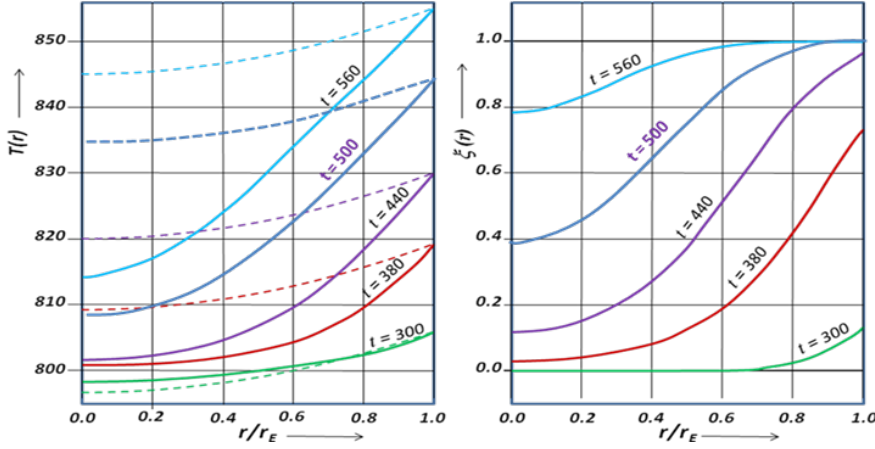
Fig. 5.8 Local temperatures $T_S(r)$ (left) and local extents of transition $\xi_r(r)$ (right) in the sample at various times according to the „continuous model" (Eq. 5.44). The transition starts at $t = 260$ s. Dashed lines in the left part represent the stabilized profiles corresponding to the given surface temperatures (without any transition).
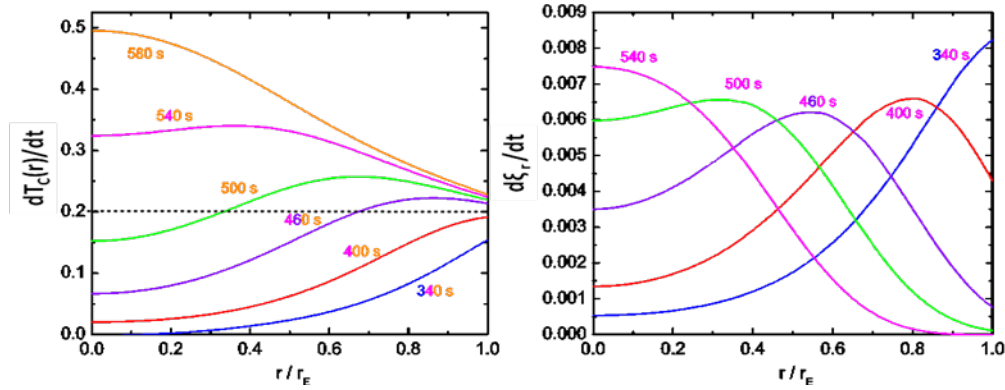
Fig. 5.9 Profiles of rates of local temperature change $dT_S(r)/dt$ (left – applied heating rate $\Phi = 0.2$ K/s as dotted line) and rates of the local extent of transition $d\xi_r(r)/dt$ (right) in the sample at various times according to the „continuous model" (Eq. 5.44)

A simultaneous solution of the differential equations (5.13) and (5.44) for the reference and the sample, respectively, under simplifying conditions $C_R = C_S$ and $\lambda_R = \lambda_S$, yields the local temperature profiles of reference $T_R(r)$ and $T_S(r)$, as well as the difference between $T_{SE} = T_S(r = r_E)$ and $T_{RE} = T_R(r = r_E)$ representing the DTA difference

$$\Delta T_{DTA} = T_{SE} - T_{RE} = T_S(r = r_E) - T_R(r = r_E) \qquad (5.45)$$

If we apply the DTA equation (5.3), which after simplification expressed by conditions $\Delta K = 0$ and $C_P^S = C_P^R$ assumes the form

$$\Delta T_{DTA} = \frac{C_P^S \dfrac{d\Delta T_{DTA}}{dt} + \Delta_t H \dfrac{d\xi_G}{dt}}{K_{DTA}} \qquad (5.46)$$

where $C_P^S = \pi r_E^2 C_S = \pi r_E^2 (C_{P,m}^S / V_m^S)$ and $\Delta_t H = \pi r_E^2 (\Delta_t H_m / V_m^S)$, we can evaluate a desmeared DTA curve corrected for the first term on the right-hand side of Eq. (5.46).

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$$\Delta T_{\text{corr}} = \Delta T_{\text{DTA}} - \frac{C_P^S \dfrac{d\Delta T_{\text{DTA}}}{dt}}{K_{\text{DTA}}} = \frac{\Delta_t H \dfrac{d\xi_G}{dt}}{K_{\text{DTA}}} \tag{5.47}$$

The mentioned correction is shown in Fig. 5.10.
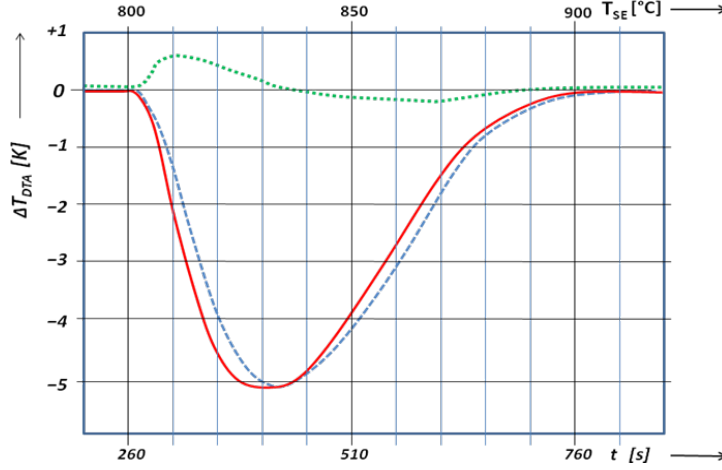
Fig. 5.10 DTA curve calculated from „continuous model" as $\Delta T_{\text{DTA}} = T_{\text{SE}} - T_{\text{RE}}$ (solid line) and the corrected (desmeared) DTA line obtained as ΔT_{corr} through Eq. 5.47 (dashed line). Dotted line represents the correction term $C_P^S (d\Delta T_{\text{DTA}}/dt)/K_{\text{DTA}}$.

However, a properly desmeared DTA curve should correspond to the relation

$$\Delta T_{\text{prop}} = \Delta_t H \frac{d\xi_G}{dt} \frac{1}{K_{\text{DTA}}} \tag{5.48}$$

where the value of global (overall) extent of transition ξ_G of the cylinder-shaped sample is given as the integral

$$\xi_G = \frac{1}{r_E^2} \int_0^{r_E} \xi_r(r) r \, dr \tag{5.49}$$

and, correspondingly,

$$\frac{d\xi_G}{dt} = \frac{1}{r_E^2} \int_0^{r_E} \frac{d\xi_r(r)}{dt} r \, dr \tag{5.50}$$

Substituting $(d\xi_G/dt)$ as obtained by integration (5.50) into (5.48) and subtracting ΔT_{prop} from data calculated by „continuous model" (see right panel of Fig. 5.9) it provides an evidently different „correction curve" compared to Eq. (5.47) as shown in Figure 5.11. This difference between „on-surface-measured" DTA and the „ideal" DTA curve should be determined as

$$\Delta T_{\text{DTA}} - \Delta T_{\text{prop}} = \int_0^{r_E} \left[\frac{dT_S(r)}{dt} - \frac{dT_R(r)}{dt} \right] r \, dr \tag{5.51}$$
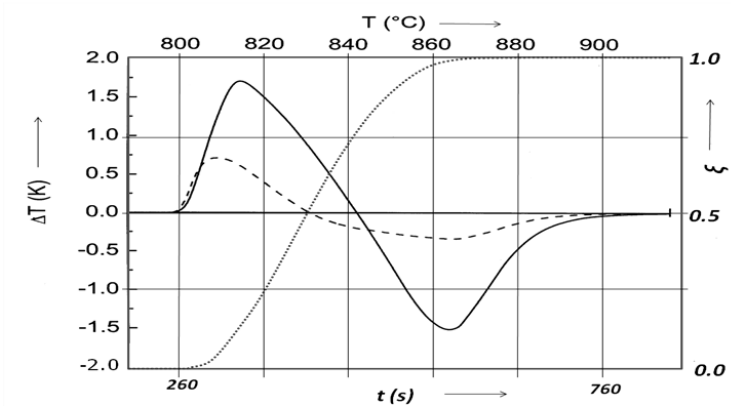
Fig. 5.11 Correction curves obtained from „DTA equation" Eq. 5.47 using differences of surface temperatures (dashed line: ΔTcorr – ΔT_{DTA}) and from Eq. 5.51 using differences between temperature integrals (solid line: $\Delta T_{\text{prop}} - \Delta T_{\text{DTA}}$). The corresponding evolution of an integral (global) extent of conversion ξ_{G} is shown by dotted curve.
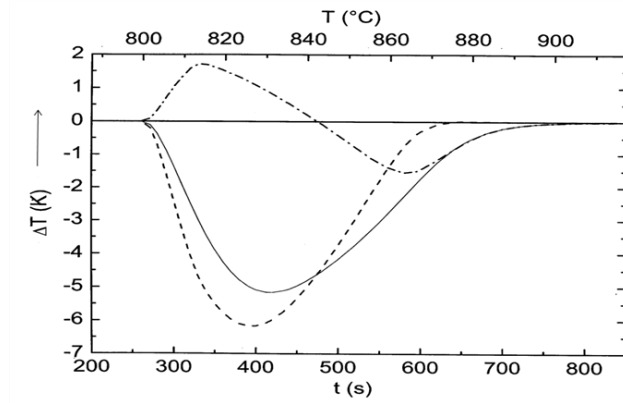
Fig. 5.12 DTA curve (ΔT_{DTA}) obtained from continuous model (solid line: ΔT_{DTA}), correction line obtained from integral temperature differences (dot-dashed line: $\Delta T_{\text{prop}} - \Delta T_{\text{DTA}}$) and the „properly corrected" DTA curve (ΔT_{prop})

Comparing Fig. 5.12 and Fig. 5.10 the conclusion follows – *the correction of DTA curves derived from temperatures measured on the surface of samples can be insufficient with respect to the correction necessary to find the actual (true) course of the process (transition) under study.*

5.4.2 Discontinuous model of a phase transition

A discontinuous model of phase transition can be suggested based on the idea of moving interface between the initial and the final phase. The interface formed by a cylindrical surface with a radius r_{t} moving from external surface (at $r_{\text{t}} = r_{\text{E}}$) to the center ($r_{\text{t}} = 0$) separates the transformed part of sample (final phase φ_{f}) from the untransformed part (initial phase φ_{f}). In the simplest model the temperature of the interface (at $r = r_{\text{t}}$) is equal to the temperature of equilibrium transition T_{t}. The temperatures $T_{\text{f}}(r)$ in the transformed part ($r_{\text{E}} > r > r_{\text{t}}$) are higher than T_{t}, while temperatures $T_{\text{i}}(r)$ in the untransformed part ($r_{\text{t}} > r > 0$) are lower than T_{t}.

If the interface propagation rate is dr_{t}/dt (with a negative value as r_{t} is decreasing during the transition) then the rate of the global extent of transition $d\xi_{\text{G}}/dt$ equals to

$$\frac{d\xi_{\text{G}}}{dt} = -\frac{2}{r_{\text{E}}^2} r_{\text{t}} \left(\frac{dr_{\text{t}}}{dt} \right) \tag{5.52},$$

as the ratio of the transformed volume of sample V_f to the whole sample volume V_S is given by

$$\frac{V_f}{V_S} = \frac{\pi(r_E^2 - r_t^2)}{\pi r_E^2} = 1 - \frac{r_t^2}{r_E^2} = \xi_G \qquad (5.53)$$

The heat flux $\dot{q}_{SE}$ is coming into the sample through the external surface at a temperature T_{SE}

$$\dot{q}_{SE} = K_{DTA}(T_W - T_{SE}) = 2\pi r_E g_{SE} \lambda_S \qquad (5.54)$$

where g_{SE} represents the temperature gradient in the sample right on the external surface. This heat flux is then consumed

  a) to increase the temperature field $T_f(r)$ in the transformed part of sample (consumed flux $\dot{q}_{cf}$),
  b) to supply the heat for the endothermic transition taking place at temperature T_t (consumed flux $\dot{q}_{ct}$) and
  c) to increase the temperature field $T_i(r)$ in the untransformed part of sample (consumed flux $\dot{q}_{ci}$)

so that

$$\dot{q}_{SE} = \dot{q}_{cf} + \dot{q}_{ct} + \dot{q}_{ci} \qquad (5.55)$$

where the respective fluxes are given by

$$\dot{q}_{cf} = 2\pi C_S \int_{r_t}^{r_E} \left(\frac{dT_f(r)}{dt} \right) r\, dr \qquad (5.56)$$

$$\dot{q}_{ct} = 2\pi \Delta H r_t \left(\frac{dr_t}{dt} \right) = \Delta H \frac{d\xi_G}{dt} \qquad (5.57)$$

$$\dot{q}_{ci} = 2\pi C_S \int_{0}^{r_t} \frac{dT_i(r)}{dt} r\, dr \qquad (5.58)$$

On the other hand the heat flux $\dot{q}_{ft}$ coming from transformed (final) phase to the moving interface is determined as

$$\dot{q}_{ft} = 2\pi r_t g_{ft} \lambda_S = \dot{q}_{ct} + \dot{q}_{ci} \qquad (5.59)$$

where $g_{ft} = (dT_f(r)/dr)_{r=r_t}$ and the heat flux $\dot{q}_{ft}$ leaving the interface into the untransformed (initial) phase is given by

$$\dot{q}_{it} = 2\pi r_t g_{it} \lambda_S = \dot{q}_{ci} \qquad (5.60)$$

where $g_{it} = (dT_i(r)/dr)_{r=r_t}$.
  Combining (5.54–5.59)

$$\dot{q}_{SE} = \dot{q}_{cf} + \dot{q}_{ft} \quad \leftrightarrow \quad 2\pi r_E g_{SE} \lambda_S = 2\pi r_t g_{ft} \lambda_S + 2\pi C_S \int_{r_t}^{r_E} \frac{dT_f(r)}{dt} r\, dr \qquad (5.61)$$

$$\dot{q}_{cf} = \frac{1}{\alpha_S} \int_{r_t}^{r_E} \frac{dT_f(r)}{dt} r\, dr = r_E g_{SE} - r_t g_{ft} \qquad (5.62)$$
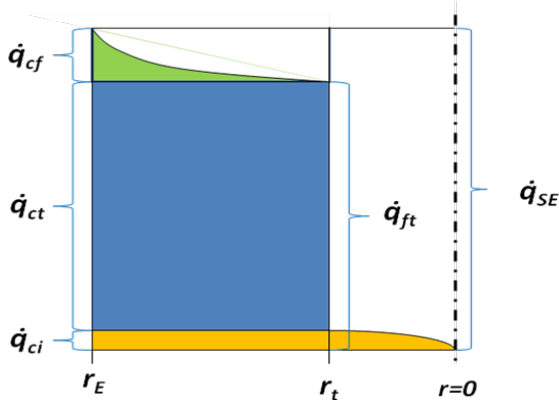
Fig. 5.13 Heat flux profiles in a cylindrical sample during transition according to discontinuous model

Dividing expressions for local heat fluxes by the local perimeter $2\pi r$ and by the thermal conductivity λ_S, the expression for local temperature gradient in the transformed (final) phase $g_f(r)$ is obtained as:

$$g_f(r) = \frac{\dot{q}_{ft}}{2\pi r \lambda_S} + \frac{1}{r\alpha_S}\int_{r_t}^{r}\Phi_f(r)\,r\,dr$$

or with respect to (5.60) as

$$g_f(r) = \frac{1}{r}\left[r_t g_{ft} + \frac{1}{\alpha_S}\int_{r_t}^{r}\Phi_f(r)r\,dr\right] \tag{5.63}$$

where $\Phi_f(r) = (dT_f(r)/dt)$. Similarly, for the local temperature gradient in the untransformed (initial) phase $g_i(r)$ as

$$g_i(r) = \frac{1}{r\alpha_S}\int_{0}^{r}\Phi_i(r)\,r\,dr \tag{5.64}$$

where $\Phi_i(r) = (dT_i(r)/dt)$.

To estimate the temperature profile in the transformed part of the sample during a transition with moving interface a simple approximation can be used for the dependence of $\Phi_f(r)$ in the form

$$\Phi_f(r) = \Phi_{SE}\frac{r - r_t}{r_E - r_t} \tag{5.65}$$

based on the assumption the heating rate is a linear function of radius r with the maximum heating rate at $r = r_E$: $\Phi_f(r_E) = \Phi_{SE} \equiv (dT_{SE}/dt) = \Phi_{RE} + d\Delta T_{DTA}/dt$ and the minimum heating rate at $r = r_t$: $\Phi_f(r_t) = 0$. The integral in (5.63) is then determined as

$$\int_{r_t}^{r}\Phi_f(r)\,r\,dr = \frac{\Phi_{SE}}{6\alpha_S}\frac{2r^3 - 3r^2 r_t + r_t^3}{r_E - r_t} \tag{5.66}$$

so that the gradient $g_f(r)$ is given as

$$g_f(r) = \frac{r_t g_{ft}}{r} + \Phi_{SE} \frac{2r^2 - 3rr_t + r_t^3/r}{6\alpha_S(r_E - r_t)} \qquad (5.67)$$

The corresponding temperature profile $T_f(r)$ should be then obtained by integration $g_f(r)$ from r_t to r with the equilibrium transition temperature T_t considered as an integration constant:

$$T_f(r) = \int_{r_t}^{t} \frac{dT_f(r)}{dr} dr + T_t = \int_{r_t}^{t} g_f(r)dr + T_t$$

$$T_f(r) = r_t g_{ft} \ln(r/r_t) +$$
$$+ \frac{\Phi_{SE}}{6\alpha_S(r_E - r_t)} \left[r^2(4r - 9r_t) + r_t^3(5 + 6\ln(r/r_t)) \right] + T_t \qquad (5.68)$$

From the boundary condition $T_f(r_E) = T_{SE}$ we have

$$T_{SE} = r_t g_{ft} \ln(r_E/r_t) +$$
$$+ \frac{\Phi_{SE}}{6\alpha_S(r_E - r_t)} \left[r_E^2(4r_E - 9r_t) + r_t^3(5 + 6\ln(r_E/r_t)) \right] + T_t \qquad (5.69)$$

Similarly, to estimate the temperature profile in the untransformed part of the sample during a transition with the moving interface the approximation can be used for the dependence $\Phi_i(r)$ in the form

$$\Phi_i(r) = \Phi_C(1 - r/r_t) \qquad (5.70)$$

based on the consideration that the heating rate is a linear function of the radius r with a maximum heating rate at $r = 0$: $\Phi_i(r = 0) = \Phi_C \equiv (dT_C/dt)$ and a minimum heating rate at $r = r_t$: $\Phi_i(r_t) = 0$. Equation (5.63) yields after integration with the substituted $\Phi_i(r)$

$$g_i(r) = \frac{1}{r\alpha_S} \int_0^r \Phi_i(r)\,r\,dr = \frac{\Phi_C}{rr_t\alpha_S} = \frac{r\Phi_C}{6\alpha_S} \cdot (3 - 2r/r_t) \qquad (5.71)$$

and from the value of gradient at $r = r_t$

$$g_i(r = r_t) = g_{it} = \frac{\dot{q}_{it}}{2\pi r_t \lambda_S} = \frac{r_t \Phi_C}{6\alpha_S} \cdot (3 - 2r_t/r_t) = \frac{r_t \Phi_C}{6\alpha_S} \qquad (5.72)$$

a relation for Φ_C is obtained

$$\Phi_C = \frac{6\alpha_S g_{it}}{r_t} \qquad (5.73)$$

and (5.71) can be rewritten as

$$g_i(r) = g_{it}(r/r_t) \cdot (3 - 2r/r_t) \qquad (5.74)$$

Integrating Eq. (5.74) from $r = 0$ to $r = r_t$

$$T_i(r) = T_C + g_{it}\left[\frac{3}{r_t}\frac{r^2}{2} - \frac{2}{r_t^2}\frac{r^3}{3}\right] = T_C + \frac{g_{it}}{6}\left(\frac{r}{r_t}\right)^2[9r_t - 4r] \qquad (5.75)$$

where T_C is an integration constant obtainable from the boundary condition $T_i(r_t) = T_t$ as

$$T_C = T_t - \frac{5}{6}\cdot g_{it}r_t \qquad (5.76)$$

and Eq. (5.75) can be rewritten as

$$T_i(r) = T_t + \frac{g_{it}}{6}\left[\left(\frac{r}{r_t}\right)^2(9r_t - 4r) - 5r_t\right] \qquad (5.77)$$

From the expressions for $T_f(r)$ and $T_i(r)$ the values for g_{ft} (in 5.68) and g_{it} (in 5.77) should be estimated as functions

$$g_{ft} = k_{ft}\frac{(T_{SE} - T_t)(1 - \xi_G)}{r_E - r_t} = k_{ft}\frac{T_{SE} - T_t}{r_E - r_t}\frac{r_t^2}{r_E^2} \qquad (5.78)$$

$$g_{it} = g_{i0}(1 - \xi_G) = g_{i0}\frac{r_t^2}{r_E^2} \qquad (5.79)$$

where k_{ft} is a dimensionless constant and g_{i0} is a constant of the dimension K/cm.

Using the value $k_{ft} = 5.5$ (estimated from relations between T_{SE} and T_t obtained from continuous model) $g_{i0} = 20$, and other values applied at continuous model ($r_E = 1$, $T_t = 800$ °C, $\Phi = 0.2$ K/s, $\lambda_S = 0.02$ W cm^{-1} K^{-1}, $C_{P,m}^S/V_m^S = 4$ J cm^{-3} K^{-1}, $\Delta_t H_m/V_m^S = 400$ J cm^{-3}) the local gradient profile $g(r)$ and the local temperature profile $T(r)$ were calculated for the global extent of transition $\xi_G = 0.7$ (corresponding radius of interface $r_t = 0.548$) as shown in Fig. 5.14.
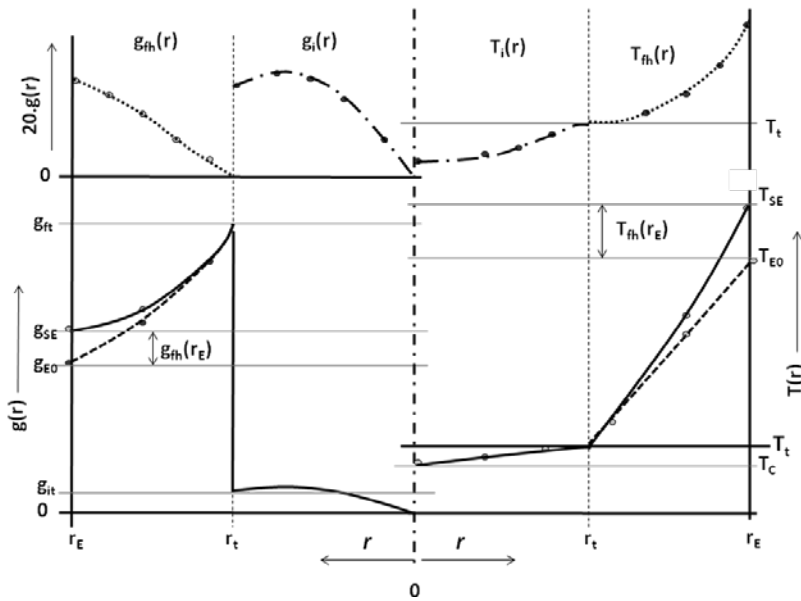
Fig. 5.14 Radial temperature gradient profile $g(r)$ (left) and local temperature profile $T(r)$ (right)

From an exact viewpoint, however, the temperature field inside a cylindrical sample during transition obeying the discontinuous model consisting of two different parts: the temperature field $T_f(r)$ inside the transformed (final) phase (at $r \in (r_t, r_E)$) given by

$$\frac{d^2 T_f(r)}{dr^2} + \frac{1}{r}\frac{dT_f(r)}{dr} = \frac{1}{\alpha_S}\Phi_f(r) \tag{5.80}$$

or

$$\frac{dg_f(r)}{dr} + \frac{g_f(r)}{r} = \frac{1}{\alpha_S}\Phi_f(r) \leftrightarrow \Phi_f(r) = \alpha_S\left(\frac{dg_f(r)}{dr} + \frac{g_f(r)}{r}\right) \tag{5.81}$$

and the temperature field $T_i(r)$ inside the untransformed (initial) phase (at $r \in (r, r_t)$)

$$\frac{d^2 T_i(r)}{dr^2} + \frac{1}{r}\frac{dT_i(r)}{dr} = \frac{1}{\alpha_S}\Phi_i(r) \tag{5.82}$$

or

$$\frac{dg_i(r)}{dr} + \frac{g_i(r)}{r} = \frac{1}{\alpha_S}\Phi_i(r) \leftrightarrow \Phi_i(r) = \alpha_S\left(\frac{dg_i(r)}{dr} + \frac{g_i(r)}{r}\right) \tag{5.83}$$

Unfortunately, the exact solution of the above differential equations under the condition of a moving interface $r_t = r_t(t)$ is still not within contemporary mathematical powers of the authors. It seems that an exact solution of discontinuous model is connected with the so-called Stefan problem indicated by Lamé and Clapeyron as early as in 1831 [57] and named after Slovenian scientist Jožef Stefan (1835–1893) [58].

5.5 Temperature profile and temperature modulation

During the last decade of 20th century temperature modulated Differential Scanning Calorimetry (tm-DSC) method was developed and used [59, 60]. The question arises what happens with the temperature profile inside a material exposed to a periodically changing heating rate. Assuming no transition occurs during heating, the temperature profile should oscillate between the stabilized profiles corresponding to heating and cooling rates. The simplified idea of such oscillations is presented in Fig. 5.15.
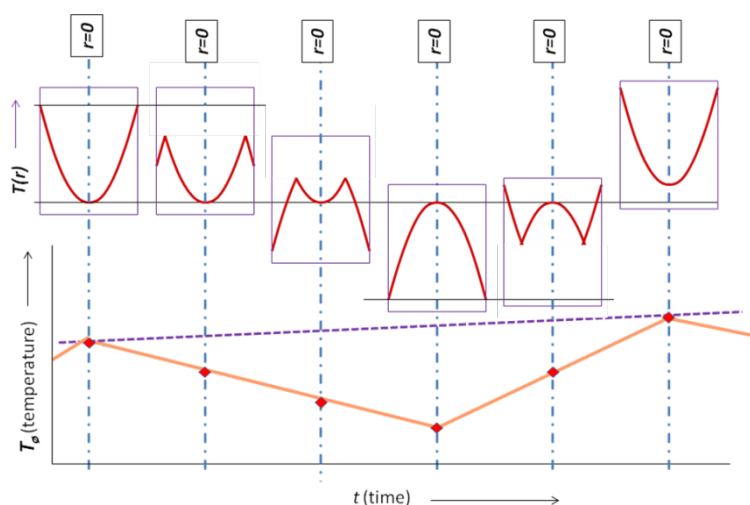
Fig. 5.15 Simplified idea of changes in temperature profile inside cylindrical sample due temperature modulation

However, the simplified idea does not respect the Fourier differential equation as expressed by Eq. (5.14). Using the above mentioned software the correct evolution of the temperature profile is more complicated as shown in Fig. 5.16.
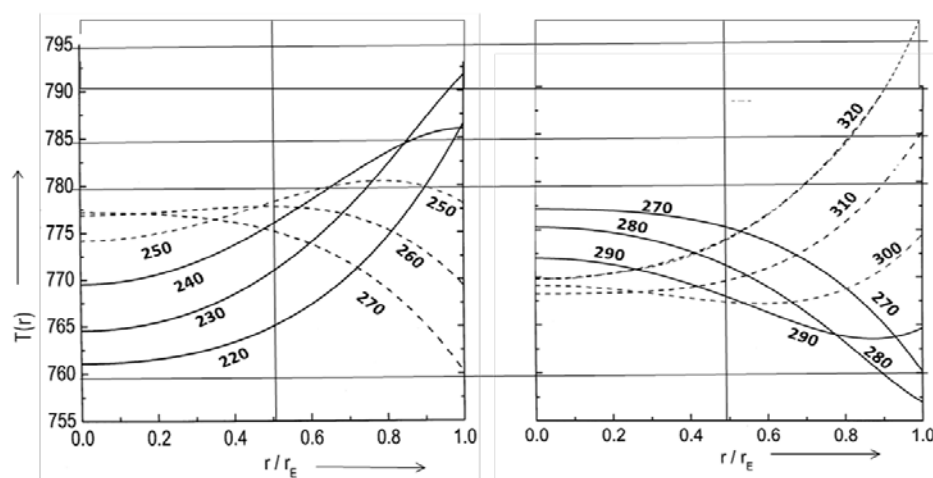
Fig. 5.16 Calculated development of temperature profile $T(r)$ during one period of temperature modulation (period $\tau = 100$ s, heating rate $\Phi = 0.1 \pm 0.6$ K/s, $\alpha_S = 0.05$ cm^2/s, $r_E = 1$ cm) for times 220–320 second

5.6 Revised DTA equation

Modern science with its emphasis on the publishable results promotes specialization. Therefore only a little account is paid to the interrelationship between various physical phenomena. This is probably the reason why most publications devoted to kinetic interpretations of curves obtained from thermal analysis ignore the delay caused by the thermal inertia of the sample, despite the fact that the correction of this distortion is known and recommended since 1967 [47].

One cause of this recent ignorance, as it appears, is a loyal confidence of scientists towards sophistication of commercial thermoanalytical devices and their manuals which make believe that the physically relevant interpre-

tation of curves of thermal analysis can be obtained by straightforward easy way. It seems that scientists believe that a mere replacement of thermocouples (in DTA) by thermocouple batteries (in heat flux DSC) or by sensitive electronic chips (in nanocalorimetry [61]) moreover renaming DTA to variously termed DSC is a sufficient solution answer. It gives an impression that the objections put forward against the use of as-measured (uncorrected-original) TA curves as the curves expressing the *authentic* rate of chemical/phase process are insignificant.

The analyses presented above confirm not only the inevitability of the earlier suggested heat inertia correction but lead also to the requirement of introducing additional correction term respecting the changes in temperature field inside the sample, which occur during the transition and/or reaction.

The analysis presented in this chapter shows, however, a more deep complexity of any kinetic studied on solid samples, where no instantaneous homogenization (stirring [32]) can be used to maintain the sample temperature constant during transition and/or reaction – the problem which could be called a *"dilemma of solid state kinetics"* [62].

Generally for any sample under study the sample temperature depends on

a) the heat transfer from or to surroundings (through the sample surface)
b) the heat consumption which is necessary to increase the sample temperature
c) the heat evolution or consumption by the reaction or transition (in the sample volume)

as it can be expressed for the sample (and its holder) in the form of infinite cylinder (with an external radius r_H) by

$$\dot{q}_{EHS} = 2\pi \left[\int_0^{r_H} C_S\left(T(r)\right) \frac{dT(r)}{dt} r\, dr + \int_0^{r_E} \Delta H\left(T(r)\right) \frac{d\xi_r(r,T(r))}{dt} r\, dr \right] \quad (5.84)$$

where $C_S(T)$ and $\Delta H(T)$ are the heat capacity of the system sample + holder and transition enthalpy change, respectively, $dT(r)/dt$ and $d\xi_r(r))/dt$ are the rates of local temperature and local extent of transition, respectively. The heat flux from/to surroundings $\dot{q}_{EH}$ depends on the temperature of the external surface of the holder T_{EH} as expressed in (5.1) $\dot{q}_{EH} = K(T_W - T_{EH})$ so that

$$\frac{K(T_W - T_{EHS})}{2\pi} = \int_0^{r_H} C_S\left(T(r)\right) \frac{dT(r)}{dt} r\, dr + \int_0^{r_E} \Delta H\left(T(r)\right) \frac{d\xi_r(r,T(r))}{dt} r\, dr \quad (5.85)$$

The first integral term represents a heat flux associated with the change of temperature field in the sample–holder system consisting of two integrals:

$$\int_0^{r_H} C_S(T) \frac{dT(r)}{dt} r\, dr = \int_0^{r_E} C_{SM}(T) \frac{dT(r)}{dt} r\, dr + \int_{r_E}^{r_H} C_H(T) \frac{dT(r)}{dt} r\, dr \quad (5.86)$$

The integrals on the right side of (5.86) can be simplified (assuming temperature independent values of C_H and C_{SM}, and zero change of heat capacity during transition) to

$$\int_0^{r_H} C_S(T) \frac{dT(r)}{dt} r\, dr = \frac{1}{2} \left[(r_H^2 - r_E^2) C_{HS} \Phi_H + r_E^2 C_{SM} \Phi_S \right] \quad (5.87)$$

where Φ_H stands for the average (over the whole volume) heating rate of the holder

$$\Phi_H = \frac{2}{r_H^2 - r_E^2} \int_{r_E}^{r_H} \frac{dT(r)}{dt} r\, dr \equiv \frac{dT_{HS\phi}}{dt} \quad (5.88)$$

where average (weighted) temperature of the holder $T_{\mathrm{HS}\phi}$ is defined as

$$T_{\mathrm{HS}\phi} \equiv \frac{2}{r_{\mathrm{H}}^2 - r_{\mathrm{E}}^2} \int_{r_{\mathrm{E}}}^{r_{\mathrm{H}}} T_{\mathrm{H}}(r)\, r\, \mathrm{d}r \qquad (5.89)$$

and Φ_{S} is the average heating rate of the sample

$$\Phi_{\mathrm{S}} = \frac{2}{r_{\mathrm{E}}^2} \int_0^{r_{\mathrm{E}}} \frac{\mathrm{d}T_{\mathrm{S}}(r)}{\mathrm{d}t}\, r\, \mathrm{d}r \equiv \frac{\mathrm{d}T_{\mathrm{S}\phi}}{\mathrm{d}t} \qquad (5.90)$$

where the average (weighted) temperature of the sample (without holder) $T_{\mathrm{S}\phi}$ is defined as

$$T_{\mathrm{S}\phi} \equiv \frac{2}{r_{\mathrm{E}}^2} \int_0^{r_{\mathrm{E}}} T_{\mathrm{S}}(r)\, r\, \mathrm{d}r \qquad (5.91)$$

Similarly the last integral on the right side of Eq. (5.85) can be simplified (assuming temperature independent value of ΔH) to

$$\int_0^{r_{\mathrm{E}}} \Delta H\left(T_{\mathrm{S}}(r)\right) \frac{\mathrm{d}\xi_{\mathrm{r}}(r, T(r))}{\mathrm{d}t}\, r\, \mathrm{d}r = \frac{r_{\mathrm{E}}^2}{2} \Delta H \frac{\mathrm{d}\xi_{\mathrm{G}}}{\mathrm{d}t} \qquad (5.92)$$

where ξ_{G} represent the average (overall) the extent of transition

$$\frac{\mathrm{d}\xi_{\mathrm{G}}}{\mathrm{d}t} \equiv \frac{2}{r_{\mathrm{E}}^2} \int_0^{r_{\mathrm{E}}} \frac{\mathrm{d}\xi_{\mathrm{r}}(r)}{\mathrm{d}t}\, r\, \mathrm{d}r \qquad (5.93)$$

Equation (5.85) is then found in the form:

$$\frac{K\left(T_{\mathrm{W}} - T_{\mathrm{EHS}}\right)}{\pi} = (r_{\mathrm{H}}^2 - r_{\mathrm{E}}^2) C_{\mathrm{HM}} \Phi_{\mathrm{HS}} + r_{\mathrm{E}}^2 C_{\mathrm{SM}} \Phi_{\mathrm{S}} + r_{\mathrm{E}}^2 \Delta H \frac{\mathrm{d}\xi_{\mathrm{G}}}{\mathrm{d}t} \qquad (5.94)$$

The dilemma of solid state kinetics stems from the fact that we are able to control the temperature T_{W} (in DTA or heat-flux DSC measurement) or the temperature T_{EH} (in compensating DSC device) but we can never control the temperature field $T(r)$ because it depends also on the evolution or consumption of heat inside the sample. Therefore, the dependence of the reaction process rate $\mathrm{d}\alpha/\mathrm{d}t \equiv \mathrm{d}\xi_{\mathrm{G}}/\mathrm{d}t$ (expressed on the basis of (5.94) assumes the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} \equiv \frac{\mathrm{d}\xi_{\mathrm{G}}}{\mathrm{d}t} = \frac{K\left(T_{\mathrm{W}} - T_{\mathrm{EHS}}\right)}{\pi r_{\mathrm{E}}^2 \Delta H} - \frac{(r_{\mathrm{H}}^2 / r_{\mathrm{E}}^2 - 1) C_{\mathrm{HM}} \Phi_{\mathrm{HS}} + C_{\mathrm{SM}} \Phi_{\mathrm{S}}}{\Delta H} \qquad (5.95)$$

where the controlled temperature is either T_{W} (in DTA experiment) or T_{EHS}. However, the temperature, which is primarily corresponding to the thermal state responsible for the transition rate is $T_{\mathrm{S}\phi}$. In a solid sample this temperature $T_{\mathrm{S}\phi}$ never subsists as an entirely independent quantity both under the linear heating rate or the so called isothermal conditions. This is substantial reason for solid-state-kinetics quandary.

If equation similar to (5.84) is applied to the reference sample:

$$\dot{q}_{\text{EHR}} = 2\pi \int\limits_{0}^{r_{\text{H}}} C_{\text{R}}\left(T(r)\right)\frac{\mathrm{d}T(r)}{\mathrm{d}t}r\,\mathrm{d}r \tag{5.96}$$

and the equation analogous to (5.94) is found in the form

$$\frac{K\left(T_{\text{W}}-T_{\text{EHR}}\right)}{\pi} = (r_{\text{H}}^2 - r_{\text{E}}^2)C_{\text{HM}}\Phi_{\text{HR}} + r_{\text{E}}^2 C_{\text{RM}}\Phi_{\text{RM}} \tag{5.97}$$

When subtracting (5.97) from (5.94) the following difference is obtained

$$\frac{K\left(T_{\text{EHS}}-T_{\text{EHR}}\right)}{\pi} = (r_{\text{H}}^2 - r_{\text{E}}^2)C_{\text{H}}\left(\Phi_{\text{HR}} - \Phi_{\text{HS}}\right) +$$
$$+ r_{\text{E}}^2\left(C_{\text{RM}}\Phi_{\text{RM}} - C_{\text{SM}}\Phi_{\text{SM}}\right) - r_{\text{E}}^2\Delta H\frac{\mathrm{d}\xi_{\text{G}}}{\mathrm{d}t} \tag{5.98}$$

where $(T_{\text{EHS}} - T_{\text{EHR}}) = \Delta T_{\text{DTA}}$. If a stabilized temperature profile is reached in the couple of reference holder–reference material, then $\Phi_{\text{HR}} = \Phi_{\text{RM}} = \mathrm{d}T_{\text{EHR}}/\mathrm{d}t = \Phi_{\text{DTA}}$, so that

$$K\Delta T_{\text{DTA}} = \left[\left(r_{\text{H}}^2 - r_{\text{E}}^2\right)C_{\text{H}} + r_{\text{E}}^2 C_{\text{RM}}\right]\Phi_{\text{DTA}} -$$
$$- \left(r_{\text{H}}^2 - r_{\text{E}}^2\right)C_{\text{H}}\Phi_{\text{HS}} - r_{\text{E}}^2 C_{\text{RM}}\Phi_{\text{SM}} - r_{\text{E}}^2\Delta H\frac{\mathrm{d}\xi_{\text{G}}}{\mathrm{d}t} \tag{5.99}$$

If the holder material (the same for sample as for reference) has a good (high) thermal conductivity then we can assume

$$\Phi_{\text{HS}} = \frac{\mathrm{d}T_{\text{EHS}}}{\mathrm{d}t} = \frac{\mathrm{d}T_{\text{EHR}}}{\mathrm{d}t} + \frac{\mathrm{d}\left(T_{\text{EHS}} - T_{\text{EHR}}\right)}{\mathrm{d}t} = \Phi_{\text{DTA}} + \frac{\mathrm{d}\Delta T_{\text{DTA}}}{\mathrm{d}t} \tag{5.100}$$

but for the rate Φ_{SM} an additional term $\mathrm{d}\theta_{\text{SM}}/\mathrm{d}t$ should be considered, being the more significant the lower is the sample thermal conductivity, such that

$$\Phi_{\text{SM}} = \Phi_{\text{DTA}} + \frac{\mathrm{d}\Delta T_{\text{DTA}}}{\mathrm{d}t} + \frac{\mathrm{d}\theta_{\text{SM}}}{\mathrm{d}t} \tag{5.101}$$

Substituting the last two equations into (5.99) the revised DTA equation is found in the form

$$K\Delta T_{\text{DTA}} = \left[(r_{\text{H}}^2 - r_{\text{E}}^2)C_{\text{H}} + r_{\text{E}}^2 C_{\text{RM}}\right]\Phi_{\text{DTA}} -$$
$$- (r_{\text{H}}^2 - r_{\text{E}}^2)C_{\text{H}}\left(\Phi_{\text{DTA}} + \frac{\mathrm{d}\Delta T_{\text{DTA}}}{\mathrm{d}t}\right) -$$
$$- r_{\text{E}}^2 C_{\text{SM}}\left(\Phi_{\text{DTA}} + \frac{\mathrm{d}\Delta T_{\text{DTA}}}{\mathrm{d}t} + \frac{\mathrm{d}\theta_{\text{SM}}}{\mathrm{d}t}\right) - r_{\text{E}}^2\Delta H\frac{\mathrm{d}\xi_{\text{G}}}{\mathrm{d}t} \tag{5.102}$$

where θ_{SM} is defined as the difference between $T_{\text{S}\phi}$ (see Eq. 5.91) and T_{EHS}

$$\theta_{\text{SM}} \equiv T_{\text{S}\phi} - T_{\text{EHS}} \tag{5.103}$$

Modifying (5.102) we can obtain

$$K\Delta T_{DTA} = \left[(r_H^2 - r_E^2)(C_H - C_H) + r_E^2(C_{RM} - C_{SM}) \right]\Phi_{DTA} -$$
$$-\left[(r_H^2 - r_E^2)C_H + r_E^2 C_{SM} \right]\frac{d\Delta T_{DTA}}{dt} - \qquad (5.104)$$
$$-r_E^2 C_{SM}\frac{d\theta_{SM}}{dt} - r_E^2\Delta H\frac{d\xi_G}{dt}$$

and then defining

$$\Delta C_\Phi \equiv r_E^2(C_{RM} - C_{SM}); \; C_\Delta \equiv (r_H^2 - r_E^2)C_H + r_E^2 C_{SM}; \; C_\theta \equiv r_E^2 C_{SM} \qquad (5.105)$$

the DTA equation with four terms on the right side is established

$$K\Delta T_{DTA} = \Delta C_\Phi\Phi_{DTA} - C_\Delta\frac{d\Delta T_{DTA}}{dt} - C_\theta\frac{d\theta_{SM}}{dt} - r_E^2\Delta H\frac{d\xi_G}{dt} \qquad (5.106)$$

The first term corresponds to the baseline part of DTA curve, the second one expresses the contribution of the heat inertia term, the third one specifies the contribution due to the changes of temperature profile inside the sample, and only the fourth term corresponds to the process occurring inside the sample. It is clear that the ratio between the second term and the last term is not diminished when the sample weight is lowered.

It should be noted that the sample heat capacity C_{SM} is changed during the transition. The simplest dependence of C_{SM} on the extent of transition ξ_G can be assumed as

$$C_{SM}(\xi_G) = C_{SMi} + \xi_G\Delta C_{SM} \qquad (5.107)$$

where C_{SMi} is the heat capacity of the initial phase and ΔC_{SM} is the integral change of sample heat capacity (i.e. the difference between heat capacities of the final and the initial phase $\Delta C_{SM} = C_{SMf} - C_{SMi}$). Considering (5.105) it follows that the first three terms on the right side of (5.106) depend on the extent of transition ξ_G.

The revised DTA equation (5.106) is valid analogously for the heat flux DSC curves (when the difference in thermoelectric signals ΔE_{DSC} is calibrated and employed instead of ΔT_{DTA}).

Another situation arises in the case of compensation DSC (e.g. Perkin-Elmer DSC method), where the temperature of sample holder is permanently kept equal to the temperature of reference holder. Then $\Phi_{HS} = \Phi_{DTA}$ in (5.100) and the second term on the right side of (5.106) vanishes. However, the third term expressing the contribution due to changes of the temperature profile inside sample stays important.

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