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From electrical analog to thermophysical modeling of DSC

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Abstract Electrical analog modeling is the conventional way for the discussion of how thermoanalytical devices work. This tradition goes back to the 50–60s of the twentieth century, when the electric circuits worked with analog signal, and RC circuits were the advanced tool for the calculation of integrals and derivatives. Today the electric circuits work with digital signal, and the computation is performed with microchips and computers. Electrical analog modeling failed to explain how DSC calibration coefficient changes with temperature. This problem was solved by means of direct thermophysical consideration. The temperature of maximum sensitivity for three DSCs is shown to obey the equation for the calibration coefficient.

Keywords Electric modeling · DSC · Thermophysical modeling · Calibration coefficient

Introduction

Traditional way in the analysis of DSC operation is to model the thermophysical device by means of an electric circuit. In this approach, the construction elements of a DSC (furnace, sample holder, crucibles, etc.) are substituted with the elements of electric circuits (conductors, capacitors, inductances), and the flows of heat are substituted with electric currents in the model circuit. Such a modeling is the essential of modern thermoanalytical tradition. This approach was used for the measurements of heat of mixing using an ITC [1], the investigation of convection [2], drying grains [3], phase transition errors in heat capacity [4], design and characterization of a high-resolution heat flux sensor [5], etc.

Analysis of the profit of electric modeling for DSC operating was never made. Neither of many monographs on thermal analysis and calorimetry published for many years [6–9] deal with electric modeling, except monograph by Zielenkiewicz [10]. The monograph by Wendlandt [11] discussed the only example on the RC circuit analogy [12].

The objective of this study is to show, though in short, why, when, and how the electrical analog modeling of DSC was accepted by thermoanalytical community and what is the disadvantage of such a modeling. Alternative thermophysical approach and modeling will be shown to succeed in the solution of the problem of how the calibration coefficient of DSC depends on temperature.

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Electric modeling

Why and when the electric modeling of thermoanalytical instruments has appeared

Technological progress in the middle of twentieth century was based mainly on the electricity (light, heat, motors) and services powered with electricity (telegraph, telephone, radio, TV, radiolocation, etc.). Electric circuits were the basic elements of technique and technology of the time.

They were used even in the calculating machines. To proceed with large amount of simple calculations (addition, subtraction, multiplication, and dividing), handle mechanical machines were used, which were invented many years before. To proceed with integration and differentiation, special electric circuits with resistors, capacitors, and inductances were designed. In applying the voltage proportional to the test signal to the input of the circuit, it was possible to measure its integral or derivative at the output [13–16].

One of the first most successful commercial thermoanalytical devices, derivatograph, was designed as the electrical device with combined electric circuits. Measured values (temperature, mass, difference in temperature between sample and reference crucibles, length) were detected at once as the output signals from the derivatograph, simultaneously with their derivatives with respect to time. The differentiation of the initial signals was made by means of in-built RC circuits. The output signal was registered with analog data recorder. The differential scanning calorimeter was developed after the derivatograph, and its output signals were designed to measure and register like those in derivatograph. It was usual and conventional way to collect the readings of an analog signal from a measuring device. It was reasonable to analyze the work of DSC like derivatograph, by means of RC circuit models.

Very simple model of a DSC is shown in Fig. 1 [17]. It is too simple and cannot be used successfully for the analysis of the differences among various types of DSCs. In developing the electric modeling, the more complex electric schemes were considered. An example of such advanced modeling is shown in Fig. 2 [18]. Thermophysical model of a DSC with heat flows inside and their electric analogs is shown in Fig. 2a. The whole analog circuit is shown in Fig. 2b. Contrary to the example in Fig. 1, the authors have considered the circuit in Fig. 2b too complex for the analysis and after several simplifications came to the scheme shown in Fig. 2c. The result of the work was in the conclusion "that the resistance relating to the heat flux between the two measuring points, i.e. their interaction, has also been taken into consideration."

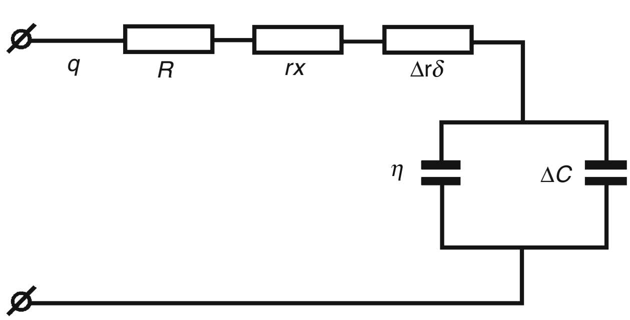

Fig. 1 The simplest electric analog circuit for DSC cell [17]

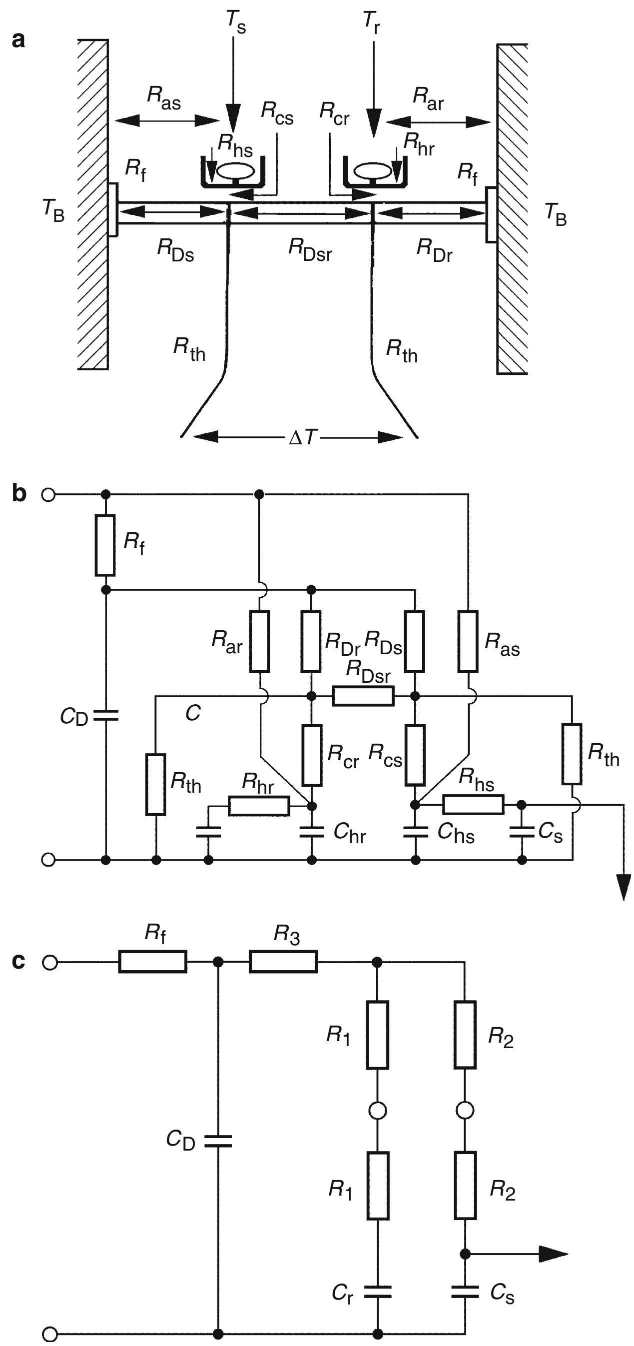

Fig. 2 Relation between elements of a DSC cell (**a**) and two electric analog models of the DSC, complex (**b**), and simplified (**c**) [18]

Progress in such a modeling is in the increase of the elements in the model circuits and the interactions among them. Most complex electric scheme of this kind we have ever seen is in the monograph by Zielenkiewicz [10], with 11 "distinguished bodies" and 32 interaction coefficients between them. One can suppose that the analysis of such complex circuit is too difficult to be proceeded without simplifications. In fact, the eleven-bodies model was simplified down to seven-bodies one [10].

Nowadays disadvantages of the electric modeling

Modern electrical engineering differs drastically from that of 50 years before. First, analog signal is substituted today with digital one. Electric circuits are rather rare in our everyday life. They are not used for the computations as microchips and computers have replaced them. Electric signals from measuring devices are transformed (integration, differentiation, etc.) digitally. Modern thermoanalytical equipment is computerized completely. Today, an electric circuit is not the suitable analog for the explanation of how thermal device works because too often it is necessary to explain how the electric circuit itself works.

Most evident disadvantage of the electric circuits in the modeling of a DSC is their irrelevance to temperature. In developing the model for a particular process in the DSC, we cannot predict quantitatively or even explain qualitatively how it will change with temperature. Resistance and electric capacity depend on temperature in completely different way as compared with thermal conductivity or radiation emissivity. After several decades of the modeling based on the electric analogy, we have no idea about the calibration coefficient of a DSC as a function of temperature. This problem is very important in differential scanning calorimetry because every DSC must be calibrated for temperature and calibration coefficient. Practical recommendations on the DSC calibration prepared by GEFTA use only empirical data fitted to a parabola over the temperature range of 100 °C (Fig. 3) [19, 20]. There is no theoretical background for the parabola fitting the calibration coefficient. Temperature interval of DSC operation is about 500–700 °C, and the parabola cannot fit the calibration coefficient with acceptable accuracy.

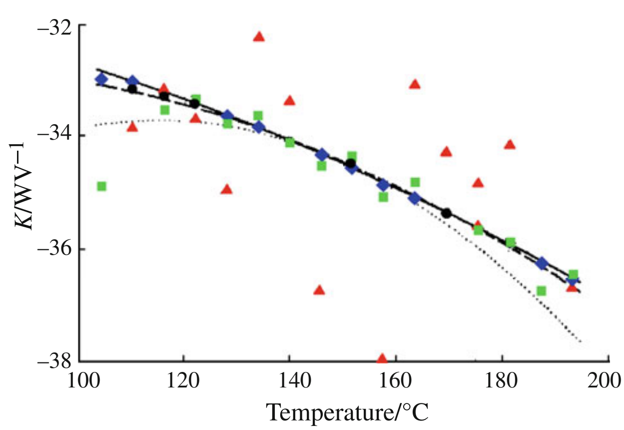

Fig. 3 Fitting empirical data on the calibration coefficient to a parabola [19]

Thermophysical model

Deriving the calibration coefficient as a function of temperature

Electric circuits cannot help us in the investigation of how the technical parameters of a DSC change with temperature. This problem can be solved after direct thermophysical consideration of the subject, and it was done recently [21]. Here we will consider the main points of the consideration and discuss how the results relate to the analysis of DSC operation.

Let us start from the analysis of heat flow in the DSC cell as it was done above for the electric modeling (see Fig. 2a), but now we will not attribute every heat flux to an element of RC circuit. Figure 4 shows that the crucibles at their positions receive the heat in two ways: (1) by thermal conductivity across the bottom from the sample holder and (2) by heat radiation onto the surface of the crucible exposed to the hot walls of the furnace. The laws of the heat exchange for these two mechanisms are different, and we should evaluate them separately. The equation for the contribution from the thermal conductivity is

$$W_{\mathrm{c}} = \mathrm{d}Q/\mathrm{d}t = -s_{\mathrm{c}}\lambda\,\nabla T, \tag{1}$$

where dQ/dt is the heat received or lost by the crucible in unit time, s_{c} is the area of the crucible bottom, λ is the coefficient of thermal conductivity, and ∇T is the temperature gradient. To proceed with the evaluations, we should define the temperature gradient, and the simplest way is to use the average value of the gradient. The latter should be averaged on the distance l from the heat source (furnace at temperature T_{f}) to the heat sink (crucible at temperature T_{i}, with i = R for the reference and i = S for the sample crucible). Thus, Eq. 1 is transformed into

$$W_{\mathrm{c}} = -\frac{s_{\mathrm{c}}\lambda}{l}(T_{\mathrm{i}} - T_{\mathrm{f}}). \tag{2}$$

Heat flow due to the radiation is

$$W_{\mathrm{r}} = -s_{\mathrm{r}}\varepsilon\sigma\left(T_{\mathrm{i}}^4 - T_{\mathrm{f}}^4\right), \tag{3}$$

where s_{r} is the area of the crucible surface exposed to the radiation, ε is the emissivity of the substance, which the crucible is made of, and σ is the Stefan's coefficient. Total heat exchange between the furnace and crucible is the sum of two contributions:

$$W_{\mathrm{R}} = W_{\mathrm{cR}} + W_{\mathrm{rR}} = -\frac{s_{\mathrm{c}}\lambda}{l}(T_{\mathrm{R}} - T_{\mathrm{f}}) - s_{\mathrm{r}}\varepsilon\sigma\left(T_{\mathrm{R}}^4 - T_{\mathrm{f}}^4\right) \tag{4}$$

for reference crucible and

$$W_{\mathrm{S}} = W_{\mathrm{cS}} + W_{\mathrm{rS}} = -\frac{s_{\mathrm{c}}\lambda}{l}(T_{\mathrm{S}} - T_{\mathrm{f}}) - s_{\mathrm{r}}\varepsilon\sigma\left(T_{\mathrm{S}}^4 - T_{\mathrm{f}}^4\right) \tag{5}$$

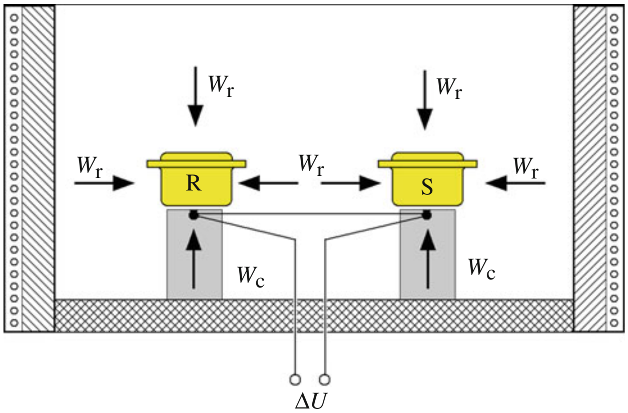

Fig. 4 Scheme of a DSC cell with reference (R) and sample (S) crucibles at their positions. Two contributions in the heating are shown with *arrows*: thermal conductivity (W_c) and radiation (W_r). Difference in temperature between the crucibles is measured by the thermocouple (ΔU)

for sample crucible. Subtracting (4) from (5), we receive the net heat flow to the sample

$$W = -\frac{s_c\lambda}{l}(T_S - T_R) - s_r\varepsilon\sigma\left(T_S^4 - T_R^4\right). \tag{6}$$

Equation becomes more convenient for use after transformation

$$\begin{aligned} T_S^4 - T_R^4 &= (T_S - T_R)\left(T_S^3 + T_S^2T_R + T_ST_R^2 + T_R^3\right) \\ &\approx 4T^3(T_S - T_R) \end{aligned} \tag{7}$$

and we have

$$W = -\left(\frac{s_c\lambda}{l} + 4s_r\varepsilon\sigma T^3\right)(T_S - T_R). \tag{8}$$

The temperature difference between reference and sample crucibles is measured with a thermocouple, and the voltage of the thermocouple is

$$\Delta U = \alpha\Delta T, \tag{9}$$

where α is the Seebeck coefficient. Finally, the heat flow to the sample is proportional to the voltage on the differential thermocouple

$$W = -\alpha^{-1}\left(\frac{s_c\lambda}{l} + 4s_r\varepsilon\sigma T^3\right)\Delta U \tag{10}$$

with the calibration coefficient

$$k = \alpha\left(\frac{s_c\lambda}{l} + 4s_r\varepsilon\sigma T^3\right)^{-1}. \tag{11}$$

The proportionality coefficient may be chosen in two equivalent forms, $A = c_B B$ and $B = c_A A$, with $c_B \cdot c_A = 1$. Defined as the calibration coefficients, they differ from one another in their dimensionality. The calibration coefficients of DSC are reported in the literature both in (power)/(voltage) and (voltage)/(power). We use here the second variant, in μV mW^{-1}. The greater the value of this calibration coefficient, the better the DSC.

Discussing the equation for the calibration coefficient

We discussed the advantages of the equation for the calibration coefficient in the previous report [21]. It was used for the development of optimal calibration procedure for DSCs of Netzsch with Proteus Analysis software [22]. Here, we will discuss how the parameters of the equation define the optimal temperature range of DSC.

Equation 11 contains three independent terms defined by (1) thermal conductivity, (2) thermal radiation, and (3) sensitivity of a thermocouple. The last point is well known, and the choice of a particular type of the thermocouple is a routine problem in thermal analysis. Approximation of the sensitivity of the thermocouple with a polynomial of temperature is to be changed for better way, but this problem is beyond the scope of this study [23]. Two first parameters are known to affect the performance of DSC, but there are no quantitative relations for these factors in the literature, and the problem is solved empirically [24]. Equation 11 contains the sum of two contributions, thermal conductivity

$$A = \frac{s_c\lambda}{l} \tag{12}$$

and radiation

$$B = 4s_r\varepsilon\sigma T^3. \tag{13}$$

The calibration coefficient is inversely proportional to the sum of these two parameters:

$$k = \alpha(A + B)^{-1}. \tag{14}$$

The decrease in the thermal conductivity increases the calibration coefficient but simultaneously increases the delay in the signal registration, i.e., makes worse the resolution in temperature. Today the temperature resolution becomes important characteristics of DSC because the trend in modern thermal analysis is the measurements at high heating rates. During the ESTAC-10, the discussion on the temperature resolution and testing procedure was between manufacturer and user of the DSC [25, 26]. In not considering the lowest temperatures where quantum effects take place, the thermal contribution, A in Eq. 14, is almost independent on temperature, while the radiation contribution increases as T^3. Inverse sum $(A + B)^{-1}$ decreases with temperature. Contrary, thermocouple sensitivity α increases with temperature like $T/(T + \Theta_V)$, where Θ_V is the characteristic temperature of the thermocouple [27]. The resulting calibration coefficient k has a maximum at moderate temperature. The lesser the contribution from radiation as compared with that from thermal conductivity, the greater the temperature of the

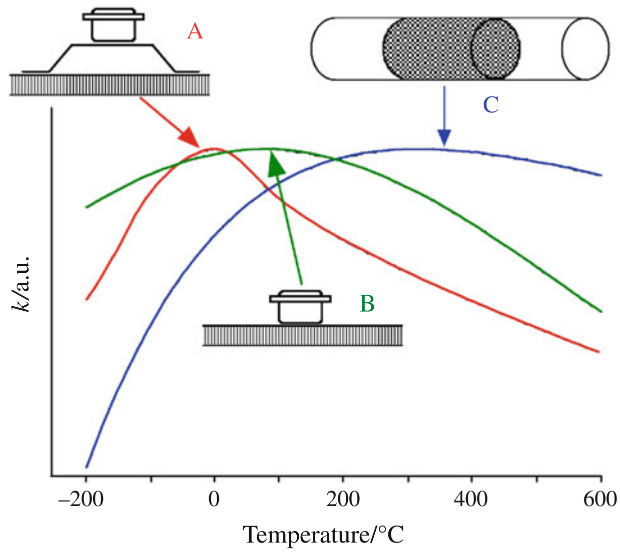

Fig. 5 Normalized calibration coefficient for three different DSCs as reported by the manufacturers: *A* DSC-30 Mettler (metal sensor), *B* DSC204 Netzsch, *C* DSC-111 Setaram. The shape of the crucibles and their positions at the sample holders are shown

maximum. This rule can be well seen in Fig. 5 where the calibration coefficients for three different DSCs are shown. Crucibles for DSC-30 Mettler (A in the Figure) and for DSC-204 Netzsch (B) are very similar in size and shape. They both are placed in similar ways with their bottoms at sample holders upright, but the sample position in DSC-30 is on the top of a flat arc, lifted above the surface of a sample holder. By this reason, the surface of the crucible is exposed to the radiation from the larger space angle. Its radiation contribution to the heat exchange is greater than that in DSC-204. The maximum of the calibration coefficient for DSC-30 is less than that for DSC-204. Crucible for DSC-111 Setaram is completely different. It is a cylinder lying sideways inside a long tube, with the whole side surface of the cylinder participating in the thermal conduction between crucible and sample holder. Here, the radiation contribution is many times less as compared with DSC-30 and DSC-204. The maximum of the calibration coefficient is the greatest for DSC-111, and its value decreases with temperature more slowly as compared with two other DSCs. Thus, the design of DSC-111 is the best for the high-temperature measurements.

Conclusions

Electrical analog modeling is shown to be out-of-date and useless for the solution of the problem of how the characteristic parameters of a DSC change with temperature. This modeling is within the tradition, but does not agree with modern technology and education.

Direct thermophysical consideration allows us to solve these problems. Equation for the calibration coefficient of a DSC was derived and shown to be useful in the analysis of suitable temperature range of operation for three DSC with various designs of the sample holder. The same approach can be very useful in the solution of other problems concerning the DSC operation.

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