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MODELLING OF QUANTITATIVE DTA EQUIPMENT I. ELECTRIC ANALOG APPROACH

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For an electric model, relationships have been established as a function of the DTA baseline shift, the intensity of the signal, the slope of the leading edge, the heating rate, the thermal resistance of the heating disc built into the DTA apparatus, the contact resistance between the disc and the sample holders, and the heat resistance between the two measuring sites. Some of the relationships obtained supported knowledge acquired earlier by other approaches, and some furnished new information. The limits of use of this simple model are indicated.

The empirical approach used earlier in the development of DTA equipment suitable for the study of enthalpy changes produced in samples by thermal treatment has been gradually replaced in the past twenty years by more exact electric analog and mathematical modelling.

Our present paper deals with the electric analog approach. This starts from the assumption that the majority of factors influencing the formation of signals obtained in DTA measurements can be converted into electric analog quantities. Moreover, their systematic experimental change is technically simple and can be achieved rapidly, so that the simulation of thermal processes and experimental conditions can be successfully realized by the study of electric circuit properties.

The thermal analogy of Ohm's law is given. I (ampere) $\approx q$ heat flux ($cal \cdot sec^{-1}$); U (volt) $\approx \Delta T$ (temperature difference), while R (Ω) $\approx R_T$ (thermal resistance). In place of $U = \frac{1}{C_{cond}} \int I \cdot dt$, the analogy of thermal capacity can be written as $T = \frac{1}{c \cdot m} \int q \cdot dt$, where c is the specific heat, m is the mass of the sample, and $c \cdot m = C_T$ is the thermal capacity.

Several attempts are known from the literature for the electric analog modelling of DTA measurements. Some of these involve processes based on the measurement of the ΔT signal, while others are DSC methods, characterized by power compensation [1–6].

Theoretical bases for modelling were deduced by Vold [7] and Boersma [8] and later by Gray [9] by formulating the thermal model taking the thermal balances and thermal resistances into account. The latter author also derived differential equations describing the course of both DTA and DSC curves.

Baxter [1] described an electric analog circuit suitable for the description of a modern apparatus containing a heat conduction disc, in spite of the fact that he used several neglections. Moreover, he recognized that the effects of thermal resistance of the heat conducting disc and the contact resistance between the disc and the sample holder must be considered separately. However, he did not take into consideration the effect of the heat flux between sample and reference sides, did not give the solution of the differential equation describing the system, and did not perform systematic investigations.

Rouquerol has given electric analog circuits for almost all of the dynamic calorimeters described in his review [10], and clearly demonstrated thereby the differences between the devices of various constructions. The substitution scheme constructed by David [2], mirroring the classical form of DTA, is incorrect in principle, neglecting the heat flow between the two cells.

The effect of heat transfer between sample and reference cells on the shape of DTA curves has been investigated by Willmann and Endl [11] by means of electric analog simulation.

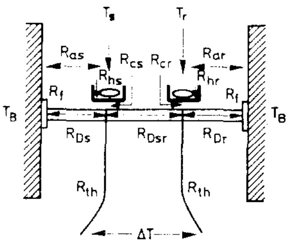

Fig. 1. Thermal block scheme of a DTA cell. Abbreviations: T = temperature; R = thermal resistance; s = sample; r = reference; f = surface of heating source (B); D = disc; h = holder; th = thermocouple; a = air; ΔT = temperature differences; c = contacts between disc and holders

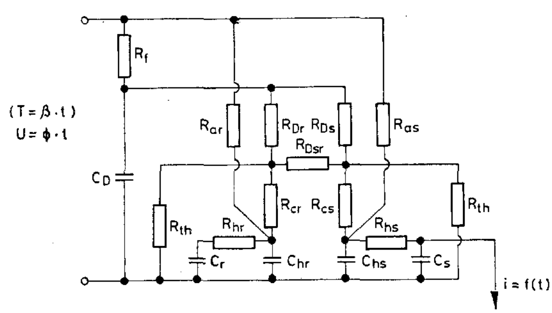

Fig. 2. Analog electric circuit of thermal block scheme (Fig. 1) R = ohmic resistance; C = = electric capacity; $\beta = \frac{dT}{dt}$; $\Phi = \frac{dU}{dt}$; i = electric current. (For others, see Fig. 1)

Special attention should be given to the work of Wilburn [3], in which, on the basis of the electric analogy of a simple but realistic thermal scheme, he elucidated the effects of the thermal capacity and heat conduction, the rate of heating and the mass of the sample on the shape of the DTA signal. However, it should be mentioned that he did not choose the site of temperature measurement in accordance with the process. In a later work [12] Wilburn et al. report on the comput-

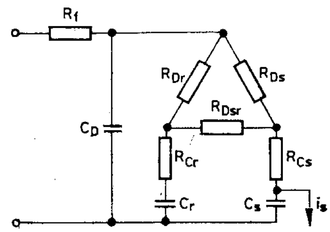

Fig. 3. Simplified electric analog circuit (see text)

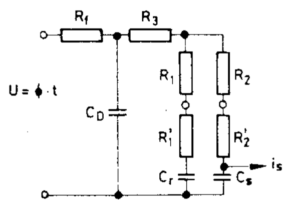

Fig. 4. Simulated model, obtained after delta asterisk transformation of circuit presented in Fig. 3

erized processing of a mathematical model, by which they derived relationships between some parameters of the sample holder and the sample, and further the area and shape of the DTA peak and the peak temperature. Moreover, they also elucidated the effect of the heat dissipation characteristics of the thermocouples.

A brief description of our relevant work has been given already [13], and our present paper will discuss our model in detail.

From a consideration of the following thermal block scheme (Fig. 1) for the process, based on the measurement of the temperature difference between the sample and the reference side, a simulating circuit (Fig. 2) has been constructed on the basis of the heat transfer characteristics.

Since our aim was only to study the heat transfer characteristics, that is to say the operation of the apparatus, we disregarded heat transfer between the sample holder and the sample, and heat transfer within the sample and reference, in compliance with the object of our work. Heat transmission through the wire of the thermocouple, and by convection and radiation was neglected, and thus the electric scheme shown in Fig. 3 was obtained, which led, after delta asterisk electric circuit transformation, to the following simulating model (Fig. 4.)

Using the Kirchhoff loop law:

$$\frac{\Phi t - U_{CD}}{R_f} = C_D \frac{dU_{CD}}{dt} + C_r \frac{dU_{Cr}}{dt} + C_s \frac{dU_{Cs}}{dt} + i_s \quad (1)$$

$$\frac{U_{Cs} - U_{Cr} - (R_1 + R_1') C_r \frac{dU_{Cr}}{dt}}{R_3} = C_r \frac{dU_{Cr}}{dt} + C_s \frac{dU_{Cs}}{dt} + i_s \quad (2)$$

From a consideration of the loop law:

$$(R_1 + R_1') C_r \frac{dU_{Cr}}{dt} + U_{Cr} = U_{Cs} + (R_2 + R_2') C_s \frac{dU_{Cs}}{dt} + (R_2 + R_2') i_s , \quad (3)$$

where $i_s = -\frac{dQ}{dt}$.

Further, under the assumption that $R_1 = R_2 = R$; $R_1' = R_2' = R_C$ (which is permissible because $R_{Dr} = R_{Ds} = R_D$ and $R_{Cr} = R_{Cs} = R_C$; that is to say the construction is symmetric), we obtain

$$U_s - U_r = R \frac{dQ}{dt} - (C_s - C_r) R \frac{dU_{Cr}}{dt} - C_s(R + R_C) \frac{d(U_s - U_r)}{dt} \quad (4)$$

This equation is similar to that introduced by Baxter [1]. The difference lies in the more complex formulation of the thermal resistance R, because re-substitution leads to

$$R = \frac{R_D + R_{Dsr}}{2R_D + R_{Dsr}}$$

meaning that the resistance relating to the heat flux between the two measuring points, i.e. their interaction, has also been taken into consideration.

For the experimental investigation of the system of differential equations given, the most simple thermal process, the solid-liquid phase transition, was selected.

The phase transition process can be divided into three periods:

I. Heating-up period, i.e. the heating of the sample from the initial temperature to the transition temperature, at a rate according to the given program.

II. The period of transformation, characterized by the constant temperature of the sample.

III. Readjustment period, during which the temperature of the sample rises again according to the given temperature program.

During electric analog modelling, the following boundary conditions are valid for these periods:

I. Heating-up period: $i_s = 0$

lower limit: $t_0 = 0$; $U_{Cr} = U_{Cs} = 0$
upper limit: $U_{Cs} = U_{Cs}^*$

II. Transformation period:

$$U_{Cs} = U^*_{Cs}, \text{ hence} \frac{dU_{Cs}}{dt} = 0$$

lower limit: $t_0 = t_I$; $U_{Cr} = U_{Cr}(t_I)$; $U_{Cs} = U^*_{Cs}$

upper limit: $\int_{t_I}^{t_{II}} i(t)dt = Q$

III. Readjustment period: $i_s = 0$

lower limit: $t_0 = t_{II}$; $U_{Cr} = U_{Cr}(t_{II})$; $U_{Cs} = U^*_{Cs}$

upper limit: $\frac{d(U_s - U_r)}{dt} = 0$

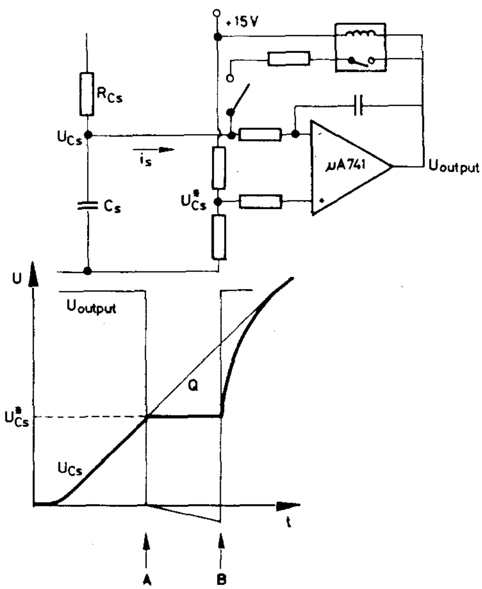

Fig. 5. Electric loop for simulation of melting process. Q = charge amount representing the enthalpy consumption of the melting process, A = the relay closes thermal resets B = manual reset

In the analog electric circuit constructed, the melting process has been simulated with the voltage stabilizer connected as shown in Fig. 5. With the aid of this circuit, with the charge quantity (Q) being nearly proportional to the melting heat, this latter could be exactly and easily simulated.

Conclusions

With systematic changes in the values of the individual simulating electric circuit elements during our experiments, their effects on the "simulated DTA peak" have been investigated, and within this the extent of the baseline displacement, the slope of the leading edge of the peak, and the dependence of the peak area have been studied. The data obtained are not absolute values, but they make possible the recognition and evaluation of tendencies.

The extent of the baseline displacement according to our investigations

a. is directly proportional to the difference in the thermal capacities of the sample and the reference;

b. is proportional to the rate of heating;

c. is not affected by the contact resistance R_C;

d. increases nearly prportionally to the increase in thermal resistance between the heating block and the measuring points, and between the two measuring points, while at the same time the resolving power decreases.

In Figs 6 *a*, *b* and *c*, relationships relevant to the shape of the DTA peak are demonstrated. The sensitivity of measurement does not change with increasing heating rate, but the leading edge of the peak becomes steeper. Regrettably, our electric analog model did not give adequate information on the time of return to the baseline, i.e. no appropriate information has been obtained on the resolving power. It has been established that the slope of the leading edge is changed mainly by R_C, $R_{D_{sr}}$ and R_D, but R_C changes it in the contrary sense to the others.

With increasing R_C, the sensitivity of measurement decreases slightly and non-linearly, while it increases proportionally with increasing $R_{D_{sr}}$ and R_D.

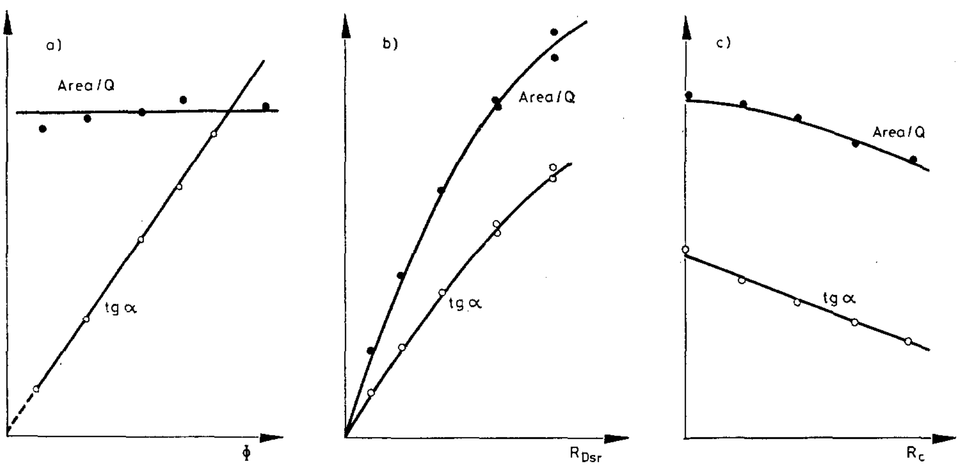

Fig. 6. Effect of heating rate (Φ) (*a*), $R_{D_{sr}}$ (*b*), and R_C (*c*) on the sensitivity of measurement (●) and on the slope of the leading edge of simulated DTA curves (○)

We would like to point out that our modelling approach permits the establishment of tendencies for design work, but does not yield numerical relationships. One reason for this is that in our model only "concentrated" R_D and C_D elements have been taken into consideration, though these do not accurately represent the actual conditions. A closer approach can be obtained if the gradients existing in the system are taken into consideration through a series of elementary cells. This would have required the complicated assembling in a suitable form of more than ten, or possibly a hundred resistances and capacitances. However, in a construction of this kind the advantage of simplicity would have been lost. Accordingly, it seemed expedient to undertake a computer simulation. As a continaution of this paper, results obtained in this study will be reported in the near future.

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RÉSUMÉ — A l'aide d'un modèle électrique, on a établi des relations décrivant l'influence de la dérive de la ligne de base ATD, de l'intensité du signal, de la pente du bord du pic, de la vitesse de chauffage, de la résistance thermique du disque de chauffage incorporé dans l'appareil ATD, de la résistance de contact entre le disque et les porte-échantillons et enfin, de la résistance thermique entre les deux points de mesure. Une partie des relations obtenues confirme les connaissances déjà acquises par d'autres approches, l'autre partie fournit des renseignements nouveaux. Les limites d'utilisation de ce modèle simple sont indiquées.

ZUSAMMENFASSUNG — Unter Anwendung eines elektrischen Modells wurden Zusammenhänge als Funktion der Verschiebung der Basislinie der DTA, der Signalintensität, der Steile der Leitkante, der Aufheizgeschwindigkeit, des Wärmewiderstandes der in das DTA-Gerät eingebauten Heizscheibe, des Kontaktwiderstandes, zwischen Scheibe und Probenbehälter und des Wärmewiderstandes zwischen den beiden Meßstellen ermittelt. Ein Teil der erhaltenen Zusammenhänge bestätigte von anderen Annäherungen her bereits vorliegende Kenntnisse, ein anderer Teil lieferte neue Informationen. Auf die Grenzen und der Nutzen dieses einfachen Modells wurden hingewiesen.

Резюме — Используя электрическую модель, были установлены зависимости как функция сдвига базисной линии ДТА, интенсивность сигнала, наклон направляющей призмы коромысла весов, скорость нагрева, термическое сопротивление нагревательного диска, встроенного в ДТА прибор, контактное сопротивление между диском и держателями образцов и тепловое сопротивление между измеряемыми местами. Одна часть полученных соотношений подтверждается знанием уже достигнутым с помощью других приближений, а другая — представляет новую информацию. Указаны ограничения использования этой простой модели.