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ADVANTAGES OF A SPHERICAL SAMPLE AT THERMAL INVESTIGATIONS OF PHASE TRANSITIONS

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Abstract: The influence of spherical geometry of a sample, on accuracy of calorimetric measurements, is considered. It is shown, that unfavourable influence of sample low thermal diffusivity, is less expressed for such a geometry, than for whatever other, previously investigated.

1. Introduction

Accurate specific heat capacity and latent heat measurements are very important in investigations of different phase transitions. Therefore, many various calorimetric techniques are rather well developed[1]. But efforts still exist for certain improvements[1,2,3] especially for samples of low thermal diffusivity, which cause considerable difficulties or inaccuracies of measurements[4,5]. Our method has been developed analysing an essential part of calorimeter as an equivalent circuit with distributed resistance-capacitance elements[6]. Influences of different geometries and thermal resistance of the sample, as well as of other parasitic resistances and capacities of the specimen, are numerically analyzed. Theoretically predicted response of the specimen to a step-like heat pulse has been confirmed experimentally[7]. Extending those previous analysis, of linear L, cylindrical C and inverse cylindrical IC geometries to a spherical one S, properties of few variants of the real thermal system are discussed and its optimal performance is suggested.

2. Temperature-time response of the specimen.

A sample of low thermal diffusivity $\underline{a}$ [8] has finite thermal resistance r_s. Therefore, a sample, as heat capacity c_s, can be divided into many layer-parts of the characteristic depth l_o, connected mutually by resistance-parts of equaly depth, along which temperature gradient will appear due to a heat flow ϕ, penetrating from input surface of the sample toward its interior. So, a ball-shaped sample can be divided into n+1 cospherical shells and simultaneously into n resistance shells. Their equal depths l_o are small for low $\underline{a}$ and fast variation of ϕ. Correspondingly, a line of $n \gg 1$ $r_i c_i$ elements[9], as in

Fig.1, will be, to a good approximation, equivalent to the real sample. Particular elements for S system can be expressed by

$$r_i = r_s/(n+1-i)^2 \Sigma_1^n k^{-2} \qquad (1)$$

$$c_i = c_s(3(n-i)(n-i+1)+1)/(n+1)^3 \qquad (2)$$

Above relations properly describe shell-capacities, falling down from the maximum input value c_o at the surface of the sample to the minimal one c_n at its center, with shell-resistances increasing from r_1 to r_n, respectively. Input resistance

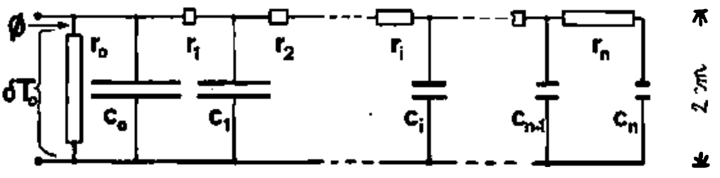

Fig.1 An equivalent circuit for the low diffusivity sample-to-sink system.

r_o in Fig.1 results from parallel combination of the heater and thermocouple leads, by which the sample is connected to the thermal sink.

An equivalent increase of temperature at the sample surface, above that of the sink, up to final value $\Delta T = \phi r_o$, can be obtained in an analytical form

$$\delta T_o = \Delta T(1 + \Sigma_1^n D_i e^{\alpha_i t}) \qquad (3)$$

solving a polynomial equation of the (n+1)-st degree

$$1 + \Sigma_1^{n+1} \tau_i^i \alpha_i^i = 0 \qquad (4)$$

and a system of (n+1) independent linear equations

$$\Sigma_1^{n+1} B_i = -1 \quad ; \Sigma_1^{n+1} B_i \alpha_i^{n+1-j} = 0 \qquad (5)$$

for j=n,n-1,...2,1, and with $D_i = B_i(1 + \Sigma_1^n \tau_j^j \alpha_i^j)$.

Coefficients τ_j^j and τ_i^i can be generally determined by rather complicated sums of definite product combinations of $r_i c_j$ elements[7], defined by eqs.(1) and (2). Above procedure is performed by computer calculations for n=12 which is great enough, following from previous results of eqs.(4) and (5) for other geometries[7]. The main result for $r_s < r_o$ is, that the response (eq.(3)) consists only one exponential term of large relative amplitude $D_1 = -(1-d)$ with large time constant $\alpha_1^{-1} = \tau_{so}$. The others have considerably smaller values, characterized by their sums $\Sigma_2^{n+1} D_i = d$ and $\Sigma_2^{n+1} \alpha_i^{-1} \simeq \tau_{si}$, due to the internal relaxation of the specimen itself. The required time constant $\tau = r_o c_o$, of an ideal specimen-to-sink relaxation, is included in

$\tilde{\tau}_{so}=\tilde{\tau}(1+\Delta)$. It is a fortunate circumstance, derived recently[7], that for the heater and thermocouple in thermal short circuit at the sample, correction term Δ, in order of few per cent, is approximately equal to total relative amplitude d of disturbing exponential terms at t=0. So, with $\tilde{\tau}_{so}$, ΔT and d determined from the recorded response of the sample, the heat capacity can be evaluated from

$$c_s \simeq \tilde{\tau}_{so}\phi / \Delta T(1+d) \quad (6)$$

with a theoretical inaccuracy, in order of promilles, equal to

$$\delta = (\Delta - d)/(1+\Delta) \quad (7)$$

It is clear, that real accuracy will be better, the smaller the magnitudes of $\tilde{\tau}_{si}/\tilde{\tau}$, Δ and δ would be obtained. They all depend on r_s/r_o, but also on thermal geometry of the system. For r_s/r_o up to 1/3, $\tilde{\tau}_{si}/\tilde{\tau}$ rises linearly, reaching about 0.5, 2.5 and 6% for S, C and L system, respectively. Comparing also Δ and δ for S system, with previous ones, presented in Fig.2, it is undoubtful, that S system is the best one among them. It has the smallest values of $\tilde{\tau}_{si}/\tilde{\tau}$ and Δ, bellow 1% even for $r_s=r_o$ (dashed curves in threefold resistance scale), and δ completely negligeable. Only the response of a cylindrical-like sample, properly arranged, could be comparable with nearly ideal response of a spherical sample.

However, situation is not so ideal, when parasitic elements are taken also into account. They are heat capacity of the heater itself, associated to c_o in equivalent circuit of Fig.1, the capacity of bonding agents and an eventual container, of a small liquid sample, c_1, with transfer resistance r_1 between them. For the same value of total specimen resistance $r_s=r_1+\Sigma_2^n r_i=$ $=r_1+r_{si}$, but including relatively larger value of r_1, Δ and δ increase toward values of unfavourable systems (S_p in Fig.2). These increases would be smaller for larger values of c_o comparing to capacity of the sample itself $c_{si}=\Sigma_2^n c_i$, with relatively smaller influence of c_1. $\tilde{\tau}_{si}/\tilde{\tau}$ will also increase with r_1/r_{si} but not so much as Δ and δ, which will be in more details considered elsewhere, along with efforts for using approximate S system in experiments.

3. Discussion and conclusion

Variations of $\tilde{\tau}_{si}/\tilde{\tau}$, Δ and δ, considering the complete specimen arrangement, through influence of equivalent $r_1 c_1$

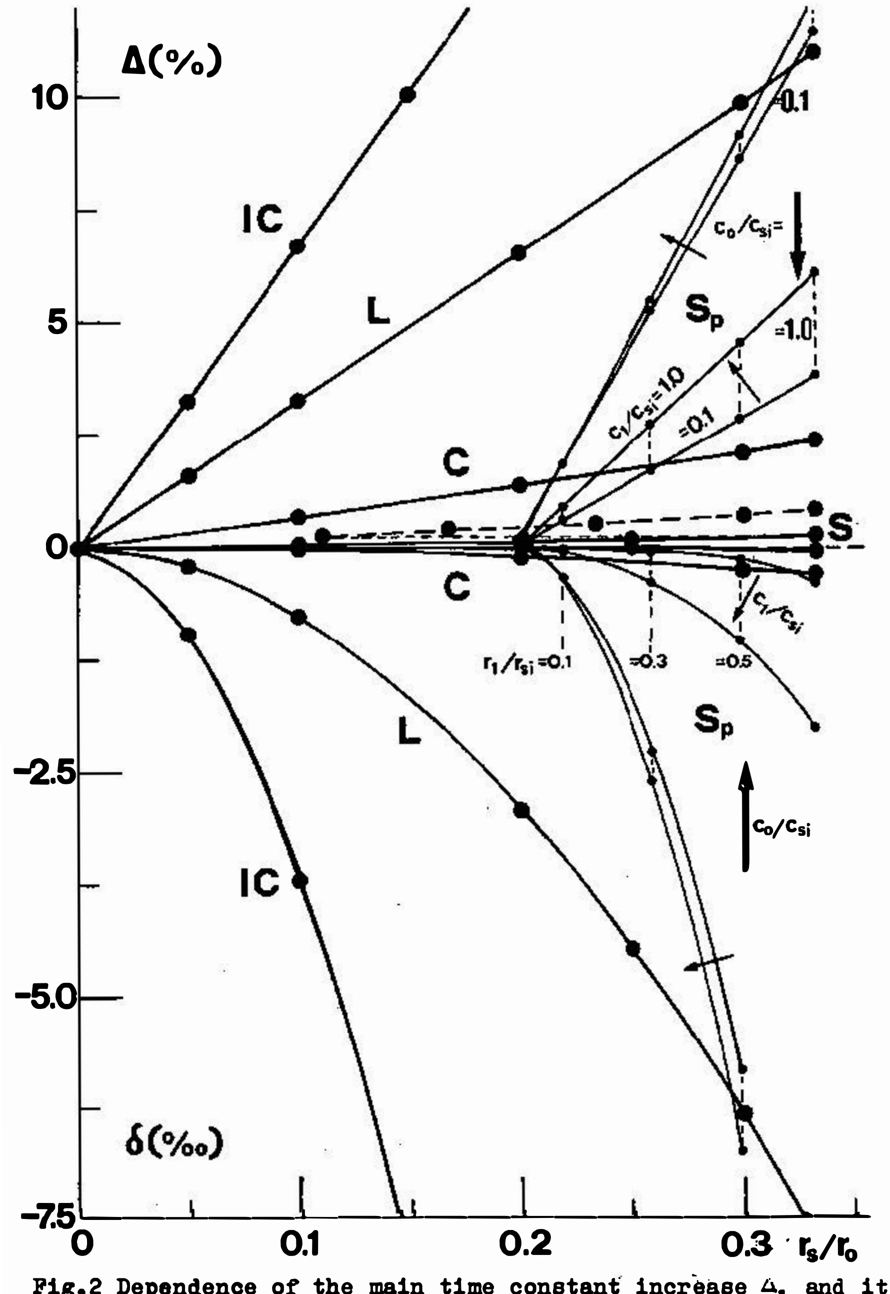

Fig.2 Dependence of the main time constant increase Δ, and its inaccuracy δ upon the thermal resistance of the specimen.

elements, show that the total thermal resistance of the specimen should be small, but also distributed in an appropriate manner. The most preferable system is with input heat capacities as large as possible, and with input thermal resistances as small as possible. It corresponds to a cylindrical or still better to an unusual spherical "thermal" geometry of the sample. However, it also includes necessarilly small transfer resistance from the heater to the sample itself, with relatively large input parasitic capacity, which could be realized using the metal container with the heater inside it, directly at the sample. Then, a nearly ideal sample response would be obtained, dependless on its low thermal diffusivity. Variation of heat capacity smaller than 10% can be detected in a narrow temperature range around phase transition, which is very difficult to realize with DTA or DSC systems[10,11]. Spherical geometry may be important also for some other calorimetric techniques like short pulse of high precision AC techniques[8,12,13], where just initial part of the response are used for heat capacity evaluation, which are for other geometries rather disturbed.

Cylindrical and spherical geometries have appropriate advantages considering accuracy of latent heat evaluation, which will be published elsewhere.

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