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DETERMINATION OF HEAT CAPACITY BY DTA. THEORY AND PRACTICE.

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For the purposes of correct mathematical description of differential curve the proper choose of the model of the thermoanalytical cell is necessary. Theoretically the simpliest model of thermoanalytical cell can be expressed by the equation. The sample under investigation is an endless cylinder with radius R, external surface of which is being heated under linear law and heating element (junction of thermocouple for example) is placed on the geometrical axis of the cylinder.

When the process becomes linear so-called "guasi-steady" condition is set in the sample, which is characterised by linear temperature increase of the all points of the sample and by stable radis gradient

$$\text{grad } T_s = \frac{BR^2}{fa_s} = \frac{BR^2}{f}\,\frac{C_s d_s}{k_s} \qquad (1)$$

where B - rate of heating (K/s), f - shape coefficient, a_s, C_s, d_s, k_s - thermal conductivity (m^2/s), heat capacity (J/g.K), density (g/m^3) and heat conductivity (J/m.K.s) correspondingly. Similar equation is to be written for an indifferent substance

$$\text{grad } T_r = \frac{BR^2}{fa_r} = \frac{BR^2}{f}\,\frac{C_r d_r}{k_r} \qquad (2)$$

Subtracting (2) from (1) we have in fact the equation of the differential line in the area, where transition in the sample is absent:

$$\Delta T = \frac{BR^2}{f}\left(\frac{C_s d_s}{k_s} - \frac{C_r d_r}{k_r} \right) \qquad (3)$$

Equation (3) is widely - known in literature on the thermal analysis. Equating with zero the rigt part of equation (3) determines thase conditious, which many investigators have been so persis tently, hopelessly and we shall add inanely striving for, i.e. that differential line in the area, where the transition is absent, would coincide strictly with the zero line:

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$$\frac{C_s d_s}{k_s} = \frac{C_r d_r}{k_r} \qquad (4)$$

Let's approximatly calculate practically possible deviation of the differential line at quasi range from zero level depending on the properties of the sample under investigation. Assume, that aluminium oxide is used as an indifferent substanse (model) also aluminium oxide is placed in the sample cell, then condition (4). Will be more or less fulfilled and the differential line will coincide strictly with zero line.

It is not difficult to calculate that the value of this deviation is not more than 1,5-2K, using literature data on aluminium oxide properties and the values of the sample radius most friquent in practice.

At least two conclusions can be drawn from even the most rough estimates:

1) appearance of large inclination or deviation of the differential line from zero line can't be related to the uncorrect choose of thermophysical properties of the model. The main reason for such defecte is an asymmetric arranqement of the sample and the model in furnace area.

2) The deviation of the differential line from the zero line under correct setting of the experiment is the quantitative value and a wish to get rid of it by way of special shoosing of model (Eq.(4)) is only voluntary (and laborius) refuse of those part of an information which is contained in the differential curve.

Consider the main conditions of correct setting of the experiment related to the quantitativė determinations of the sample heat capacity. First of all is necessary to check the quality of adjustment of the equipment. It the case of ideal adjustment the differential line coincides strictly with zero line, if there is no any substance in the sample and model cells (both cells are empty). If it is provided and reproduced rather well during repeated heatings, then one may proceed to the second stage of experiment-calibration. Fore this purpose DTA is taken off with other conditions being maximum prezerved and placing some substance with known specific heat into the sample cell.

DTA-curve will not coincide with the zero line in this case. An area between the zero line and the differential line is a measure of the heat, absorbed by the sample.

$$Q = KS \qquad (5)$$

Quantity of the heat absorbed by the sample (more exactly the difference between the quantity of the heat absorbed by the sample and by the air, wich filled the cell before) can be calculated as:

$$Q = m_r C_r (T_2 - T_1) - (T_2 - T_1) m_a C_a \qquad (6)$$

where values with the sing "r" are related to that substance with known specific heat in respect to which the calibrztion is made, the values with sing "a" are related to the air in which adjustment of the equipment was fulfilled during the previons experiment. Taking into account that C_a and C_r are usually of the same order, m_a is by three orders less, than m_r, then the second item in Eq.((6) can be often ignored:

$$Q = m_r C_r (T_2 - T_1) \qquad (7)$$

$T_2 - T_1$ - some small temperature range arbitrary chosen on the temperature axis.

Some area of the deviation of the differential line, bounded by the same temperatures T_1 and T_2, will correspond to the quantity of heat, calculated in Eq.(6):

$$S = (\Delta T_r - \Delta T_a)\,(t_2 - t_1)$$

or

$$S = \left(\Delta T_r - \frac{BR^2}{f a_a}\right)(t_2 - t_1) \qquad (8)$$

where t_2 and t_1 - momente of time (s) when T_2 and T_1 are reached, ΔT_r - DTA-curve deviation (K), a_a - thermal conductivity of air in temperature range $T_2 - T_1$ (literature data).

Substituting (7) and (8) into (5)

$$K = \frac{C_r m_r}{\dfrac{\Delta T_r}{B} - \dfrac{R^2}{f a_a}} \qquad (9)$$

The second item in the denominator of (9) can be rather often but not always ignored when using substances relatively low thermal conductivity and under temperature.

Calibration cofficient K can be estimated ussing Eq.(9) as the function of temperature in needed temperature range.

Finally the third working DTA-curve is taken when off the sample under ivestigation is placed into the cell and unknown value of specific heat capacity of the sample is calculated:

$$C_s = \frac{\left(\frac{\Delta T_s}{B} - \frac{R^2}{4a_a} \right)}{\left(\frac{\Delta T_r}{B} - \frac{R^2}{4a_a} \right)} \; \frac{m_r C_r}{m_s} \tag{10}$$

Using logic of reasoning presented above it is not difficult to derive an equation for calculation of heat capacities for case, when adjustment of the equipment is far from ideal.

The error of the heat capacity calculation when using analysed here the classic model depends first of all on the equality of the thermal conductivities of investigated and calibrating substances (Eq.(10)).

The methodics method, wich removes the relation of the calibrating coefficient to the heat conductivity is the placement of the heating element on the surface of the sample under investigation.For the model considered above it is senseless and it must be slightly complicated: the sample under investigation of radius R with the heating element placed on it's surface is placed into some cylinder (of external radius R_1) made of the material with thermophysical properties C_1, d_1, k_1.

An external surface of the cylinder is being heated under the linear law.

For this model the equation of the differential line at the quasisteady becomes:

$$\Delta T = \frac{BR^2}{2k_1} \ln R_1 / R \; (d_s C_s - d_r C_r) \tag{11}$$

The final equation similar to the Eq.(10) for the classic model can be derived from similar reasoning using the Eq.(11) instead of the Eq.(3).

Eq.(11) and accordingly the final equation don't contend the heat conductivity of neither calibrating nor investigated sample and all the other values are known (C_r), constant (R, R_1, k_1) or can be easily calculated (d_r, d_s, B) during an experiment itself.

The calculation of the heat capacities is realised in the complex "AIST" which we designed including microcomputer, display, plotter, printing unit, connection unit and DTA-7 device.