Thermochimica Acta, 92 (1985) 249-252
Elsevier Science Publishers B.V., Amsterdam

ON THE DIATHERMAL CALORIMETRY THEORY

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ABSTRACT

The calculations for the three diathermal calorimeter designs are given and their merits and dismerits are compared. The recommendations for the embodiment of the respective design versions are proposed.

INTRODUCTION

The calorimetric measurements under high temperatures involve grave experimental problems. At above 1400 K the correct thermodynamic properties evaluations are possible only with the drop calorimeters which require, however, considerable labour consumption for the experiment execution /1/. The low cost of the equipment and the labour consumption required for the experiments of this kind call forth numerous endeavours to derive the calorimetric information from the DTA curves /2,3/. The wide application of such an approach to the calorimetric measurement is restricted by rough assumption which one is compelled to accept for the description of phase transitions. The problems mentioned may be solved, in part, by the usage of diathermal calorimetry which combine in itself the advantage of the express and cheap analysis with that of the correct phase transition description /4/.

THE MATHEMATICAL MODEL

The description of the heat exchange process taking place between the diathermal shell, the surrounding medium and the calorimetric cells containing the test and reference substances, the latter being simulated by solids of concentrated parameters, involves heating in which the temperature difference between the external and the internal diathermal shell surfaces near the sample is held constant, $T_{ex}-T_s$=const. Then, for the entire process duration, independently of the process taking place in the test substance, $\mathcal{V}_1 = \mathcal{V}_2 = \mathcal{V}_3 = \ldots = \mathcal{V}_i = \mathcal{V}$ where $\mathcal{V} = \frac{\partial T}{\partial \tau}$ and "i" is the measurement site.

Proceedings of ICTA 85, Bratislava

If the diathermal shell contains only a calorimetric cell with the test substance, then the heat balance equation will be:

$$\alpha(T_{ex}-T_s)=m_sC_sv+q\frac{dm_s}{d\tau}+m_{sh}C_{sh}v+\frac{dQ_l}{d\tau} \qquad (1)$$

where α is the proportional constant, m is the mass, C is the specific latent heat of transformation, Q_1 is the heat losses, the subscripts being: s - sample and sh - shell. When the transformations are absent $\frac{dm_s}{d\tau}=0$, assigning $\frac{dQ_l}{d\tau}=q_1$ we obtain:

$$\alpha(T_{ex}-T_s)=m_sC_sv+m_{sh}C_{sh}v+q_l \qquad (2)$$

$$m_sC_s=\left[\alpha(T_{ex}-T_s)-q_l\right]/v-m_{sh}C_{sh} \qquad (3)$$

$T_{ex}-T_s$ and v should be measured for each experiment cycle and α, q_1, $m_{sh}C_{sh}$ are defined in the calibration experiment using the reference substance and empty calorimetric cell.

At $\frac{dm_s}{d\tau}\neq 0$:

$$\alpha(T_{ex}-T_s)\approx\frac{d(\Delta H_{pt})}{d\tau}+m_{sh}C_{sh}v+q_l \qquad (4)$$

and the phase transition enthalpy ΔH_{pt} is defined by the expression:

$$\Delta H_{pt}=\int_{\tau_{st}}^{\tau_{end}}\left[\alpha(T_{ex}-T_s)-m_{sh}C_{sh}v-q_l\right]d\tau \qquad (5)$$

Thus, when using one calorimetric cell containing the test substance it is necessary to construct the temperature dependence for three empirical values: α, q_1 and $m_{sh}C_{sh}$.

When applying the differential-type calorimetry an empty cell x along with the cell containing the test substance are placed into the diathermal shell. The thermal balance equation for the first is written as follows:

$$\alpha(T_{ex}-T_x)=m_{sh}C_{sh}v+q\frac{dm_s}{d\tau} \qquad (6)$$

Assuming that α, $m_{sh}C_{sh}$, q_1 are equal for both cells, we subtract the equation (6) from the equation (1):

$$\alpha(T_x-T_s)=m_sC_sv+q\frac{dm_s}{d\tau} \qquad (7)$$

The equation (7) allows to exclude the entities q_1 and $m_{sh}C_{sh}$ from the further consideration.

Consider the case of $\frac{dm_s}{d\tau}=0$, then:

$$m_s C_s = \alpha (T_x - T_s)/V \qquad (8)$$

The value of the phase transition enthalpy for the differential-type diathermal calorimeter is defined by the expression:

$$\Delta H_{pt} = \int_{\tau_{st}}^{\tau_{end}} \alpha (T_x - T_s)\, d\tau \qquad (9)$$

Thus, when using two calorimetric cells, one containing the substance to be assessed and one empty, it is necessary to deduce the temperature dependence for one empirical value, α , only. Such calibration is carried out in the experiment using the reference substance.

The output of the diathermal calorimeter could be raised by combining the calibration experiment in which the reference is used with the routine. For this end an additional cell containing the reference substance is placed into the diathermal shell, the heat balance equation of the cell being:

$$\alpha (T_{ex} - T_r) = m_r C_r V + m_{sh} C_{sh} V + q_e \qquad (10)$$

where the subscript "r" relates to the reference substance. By subtraction equation (6) from equation (10) we obtain:

$$\alpha (T_x - T_r) = m_r C_r V \qquad (11)$$

When the phase transitions are absent ($\frac{dm_s}{d\tau} = 0$) it follows from the equations (11) and (7):

$$m_s C_s = m_r C_r (T_x - T_s)/(T_x - T_r) \qquad (12)$$

The expression for the value of the phase transition enthalpy retains the form (9) in which the coefficient α could be derived from the equation (11):

$$\alpha = m_r C_r V/(T_x - T_r) \qquad (13)$$

or from the known phase transition enthalpy values for the reference substances.

The designs of the diathermal calorimeter of one, two and three cells are shown in Figs. 1,2 and 3, respectively.

CONCLUSIONS

The disadvantage of the one-cell diathermal calorimeter consists in the necessity of subsequent experiments involving the test

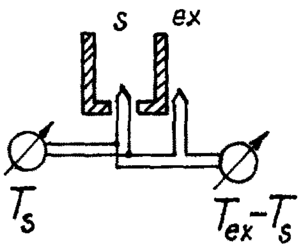

Fig.1 Scheme of one - cell diathermal calorimeter

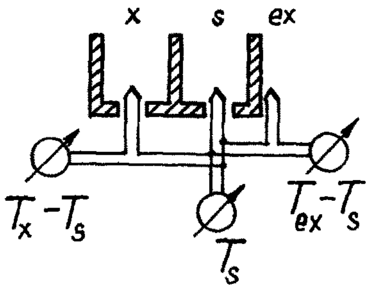

Fig.2 Scheme of two-cell diathermal calorimeter

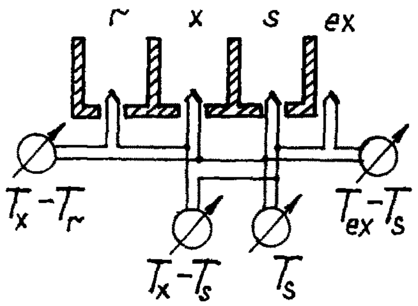

Fig.3 Scheme of three-cell diathermal calorimeter

and the reference substances and empty cell that may lead to a rather inaccurate repeatition of the heating conditions. In the case of two - and, especially, three cell-type diathermal calorimeters the identical thermal resistances of the calorimetric cells relative to the diathermal shell are strictly required. Moreover, the limited dimensions of the high temperature unit call forth design problems in providing for the monitoring unit a sufficient temperature difference between the external diathermal shell surfaces.

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