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CONTINUOUS MEASUREMENT OF HEAT CAPACITY WITH THE AID OF HEAT OSCILLATIONS IN THE TEMPERATURE RANGE FROM 25 - 500 ^{o}C

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INTRODUCTION

The determination of heat capacity and mass of a substance belongs to the most important measuring tasks for the purpose of thermal analysis. Especially the determination of these quantities as function of temperature is very informative. A method of analysis using very small samples is described below, which allows to determine these properties simultaneously with a very good sensitivity. The mass changes are not detected by weighing as with the usual thermogravimetric analysis but with the aid of the inert mass. The sample is therefore distributed at the surface of a stretched thin metal band, which is excited to autonomous vibrations.

For determination of heat capacity a modified method of alternating-current calorimetry has been developed.

The heat capacity is continuously determined by heating the substrate with an alternating current of low frequency and measuring the phase angle between the oscillating electrical power and the sinusoidal temperature fluctuations produced by the heating. The method presented allows a measurement which is nearly independent of convection and radiation.

THEORY OF THE METHOD FOR MEASURING THE HEAT CAPACITY

Figure 1 shows the scheme of the thermal system. In the heating chamber, a thin platinum foil, coated with the sample, is horizontally stretched and heated by the current I.

In the course of the experiments, the temperature of the heating chamber rises with constant rate from 25^{o}C to 500^{o}C.

On the simplifying supposition that the power supplied to the foil is dispersed to the environment by conduction, convection and radiation and partially stored in the heat capacities of foil and sample, the temperature of foil is uniform .

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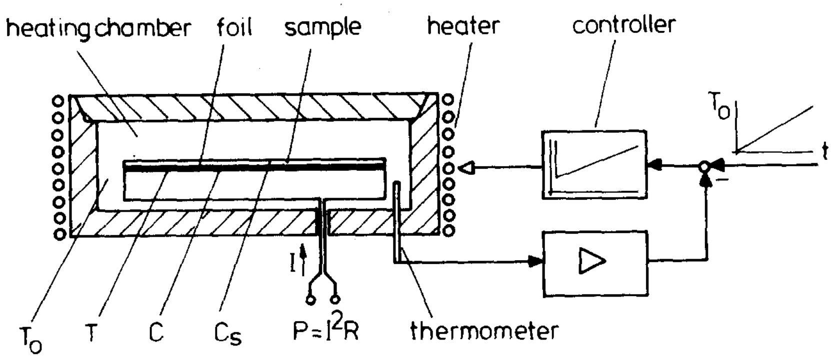

Fig. 1. Scheme of the thermal system.
T temperature of the platinum foil, T_0 temperature in the heating chamber,
C heat capacity of the platinum foil, C_0 heat capacity of the sample,
P electric power.

The temperature difference between foil and ambient air is $\vartheta = T - T_0$. On condition, that the sample represents a very thin layer, its transversal heat resistance is negligible /1/, the differential equation of the thermal system is derived from the energy balance :

$$\alpha A_0 \vartheta + \varepsilon\sigma A_0 (T^4 - T_0^4) + (C + C_S)\frac{d\vartheta}{dt} = P \qquad (1)$$

A_0 is the surface area, α the surface-heat transfer coefficient, ε the emission coefficient and σ the Stefan-Boltzmann-constant. With the allowable linearisation of heat radiation

$$T/T_0 - 1 \ll 1 \Rightarrow \varepsilon\sigma(T^4 - T_0^4) \approx \varepsilon\sigma 4 T_0^3 \vartheta = \alpha_S \vartheta \Rightarrow \alpha^* = \alpha + \alpha_S \qquad (2)$$

follows the linear differential equation (3)

$$\alpha^* A_0 \vartheta + (C + C_S)\frac{d\vartheta}{dt} = P \qquad (3)$$

If the platinum foil is supplied with a sinusoidally varying power (equation 4),

$$P = P_0(1 + \cos \omega t) \qquad (4)$$

the steady state temperature is calculated by superposition of the static part $\vartheta_0 = P_0/(\alpha^* A_0)$ and the oscillating part $\vartheta = f\,(P_0 \cos\omega t)$ of the foil temperature. To determine amplitude and phase of the fluctuating temperature, the differential equation is transformed with the aid of a complex vector formulation :

$$\underline{P} = \hat{P}_0 e^{j\omega t} \quad \text{and} \quad \underline{\vartheta} = \hat{\vartheta} e^{j\omega t} \qquad (5)$$

The solution is an algebraic equation :

$$\underline{\vartheta} = \underline{P}/(\alpha^{*}A_o + j\omega(C+C_s)) \Rightarrow \vartheta = \hat{P}_o/A \cos(\omega t + \varphi) \tag{6}$$

with $A = [(\alpha^{*}A_o)^2 + \omega^2(C+C_s)^2]^{1/2}$ and $\varphi = -\arctan[\omega(C+C_s)/(\alpha^{*}A_o)]$

Two methods are available for the determination of heat capacity :

a) Measuring the amplitude of temperature oscillation, and the phase difference between power and temperature, calculating the heat capacity by

$$C + C_S = \hat{P}_o/(\omega\hat{\vartheta}) \sin\varphi \tag{7}$$

b) Automatical determination of the stored part $\underline{P}_c$ by means of phase control. The differentiation of temperature oscillation with respect to time generates the vector $\underline{P}_k = j\omega k\vartheta$, whose phase differs from that of vector $\underline{P}_c$ by about 180^o (fig.2).

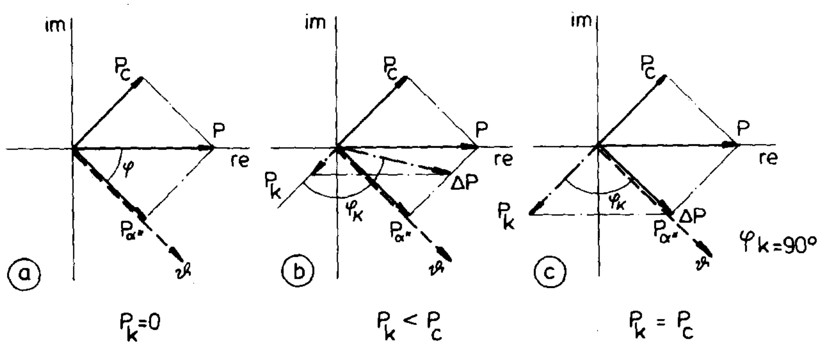

Fig. 2. Vector diagram for the determination of heat capacity.

By variation of k the phase difference φ_k between $\underline{\Delta}P = \underline{P} - \underline{P}_k$ and $\underline{P}_k$ is brought to 90^o. In this case $\underline{P}_k = \underline{P}_c$ and k is proportional to the combined heat capacity of platinum and sample

$$K \sim C + C_S \tag{8}$$

On this simplifying supposition the measured value of heat capacity is independent of frequency, convection and radiation. If the chamber temperature rises with time, measurement of C_s as a function of temperature is possible. The influence of heat conduction over the ends of the foil was reported in /2/. It results, that above a critical frequency there is no influence of conduction.

MEASURING DEVICE

Fig. 3 shows the essential part of the measuring device : The electric circuit for measuring the foil temperature with the aid of electrical resistance in the presence of a simultaneously supplied heating power.

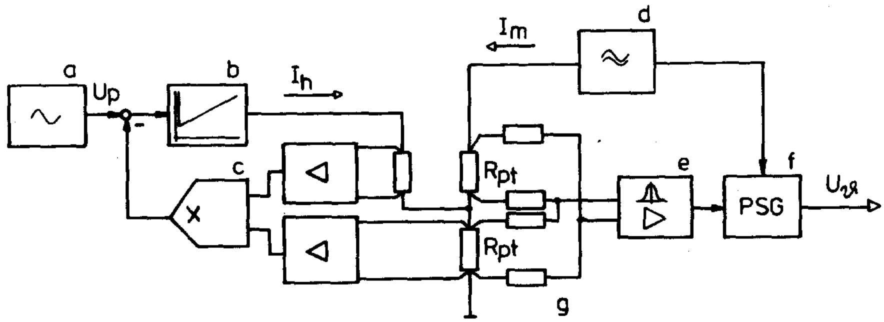

Fig. 3. Power control and measurement of temperature
a sine generator, b controller, c multiplier, d carrier-frequency generator, e sensitive amplifier, f phase sensitive rectifier

Central part of the arrangement are two platinum foils which are contained in the heating chamber side by side. One of this foils is coated with the sample to be measured. With the aid of the carrier-frequency measuring circuit, the temperature of the coated foil,which is generated by the heating current, is measured. A closed loop controls the heating current in such a way, that the electric power varies according to equation 4.

Fig. 4 shows the block diagram of the compensating method for the determination of heat capacity. For the measurement of phase, necessary for compensation, a phase sensitive rectifier is provided, whose mean value of output voltage is proportional to the cosine of the phase angle φ_k.

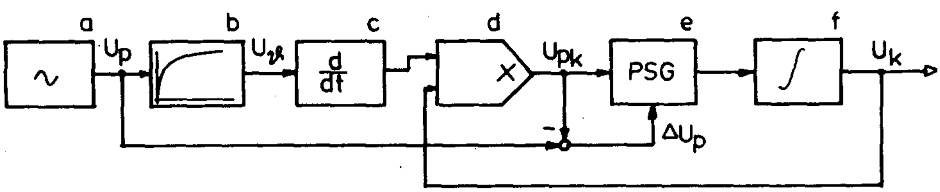

Fig. 4. Block Diagram for the determination of heat capacity
a sine generator, c thermal system, c differentiator, d multiplier,
e phase sensitive rectifier, f integrator.

The following integrator varies the input voltage U_k of the multiplier until the phase angle, between U_{pk} and U_p is 90^0. The output voltage of the integrator is then proportional to heat capacity.

MEASURING RESULTS

To show the usability and accuracy of the described measuring method, the heat capacity of the uncoated platinum foil was measured in the temperature range from 25^0C to 500^0C and compared with data from literature. Fig. 5 shows the results.

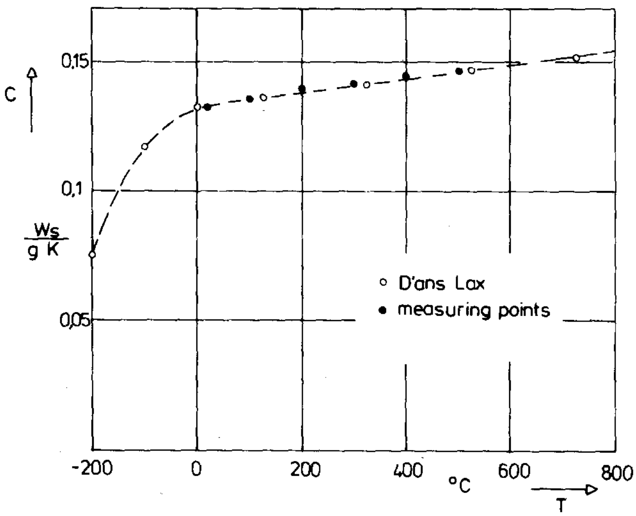

Fig. 5. Specific heat capacity of platinum

Under 350^0C the resolution of result of measurement was better than 0,2 % and above this temperature better than 0,5 %.

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