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STUDY OF THE INTERACTION BETWEEN IONIC SALTS AND WATER BY HIGH-RESOLUTION CALORIMETRY

I. Calorimeter and standard measurements

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The construction, the isothermal operation (26.2 ± 0.06) and the calibration of a differential calorimeter of high performance are described. Its construction is based on the conduction principle by using copper resistors noninductively coiled on thin aluminium cylinders used as temperature sensors with very low inertia. Thermal flows are measured by using an ac bridge with a lock-in amplifier. The calibration, both of the height (h) and of the area (A) of the recorded peaks, is performed by using calibrated heat pulses w_p with errors under 0.5%. A reproducible value of ratio h/A is obtained on a large number of w_p values, which represents a figure of merit of the high-performance calorimeter. This value is an immediate index of the nature of the general transformation process. For a clear-cut definition of the process, the universal procedure recently established on the topoenergetic principles is applied.

Calorimetry occupies a central position among analytical techniques, due to the fact that any process of transformation is accompanied by a thermal effect. From subtle nuclear reactions to complicated biological processes, calorimetry is able to reveal the energy flow and the overall energy of the triggered processes. It is noteworthy that the discovery of the neutrino particle found the strongest phenomenological support in the early calorimetric measurements [1, 2], revealing it as an inductive process.

The performance of a particular calorimeter can be experimentally evaluated according to theoretical principles, generally considering its associated energy circuit like an electric network [3–6]. The high resolution of the DTA and DSC systems actually developed is essentially due to a small heat resistance between the temperature-sensitive element and the sample, and to the use of small amounts of samples. However, these conditions do not allow the performance of reproducible experiments on a large variety of reacting systems for which the transformation process is triggered by the isothermal mixing of two or more components.

Topoenergetic working principles developed in the past decade allow the effective classification [7] and optimization [8, 9] of calorimetric measuring systems with a view to the better separation of elementary processes [10], the identification of their nature and the evaluation of the amplitude in standard units [11] and threshold temperatures [12, 13]. An important advantage of calorimetric measuring systems is the direct demonstration of the polarity of the process [14].

A high-performance calorimeter designed for both isothermal and non-isothermal operation modes is described in the present work. The main purpose arises from the necessity for solubility data standardization in a data bank created in accordance with recently-established standard experimental conditions [12, 13].

1. Calorimeter

1.1. Calorimeter vessel

The calorimeter described below has two identical measuring cells as generally used in differential calorimetric systems for an accurate baseline in isothermal and nonisothermal modes.

Figure 1 shows a cross-section of the whole calorimetric vessel. The inner brass block (1) has a lens form with a view to the better elimination of temperature gradients along its axis [15]. The sample and reference cells (7), made of aluminium, 10 mm in inner diameter, 20 mm in height and 0.2 mm in thickness of the lateral wall, are placed in tandem along this axis. On them are noninductively coiled the temperature-sensitive elements, made of 0.08 mm diameter coated copper wire (approximately 50 Ohm/20 degree each). An air layer 0.5 mm thick between the exterior wall of the cells and the brass block represents the external heat resistance of the associated energy circuit of the measuring system [7–10] (see section 2). A similar arrangement with high resolution for reacting systems with low energy flows has recently been developed [6], and is basically the same as for Perkin–Elmer DSC models except for the compensation loop [3, 7].

The temperature control is ensured by another copper resistance (coated wire 0.08 mm in diameter and approximately 500 Ohm/20 degree) as sensitive element and a heater coil made of NiCr wire 0.15 mm in diameter and approximately 250 Ohm/20 degree. Both resistances are strongly and noninductively coiled on the copper cylinder (3) by using thin layers of mica and glass fibre textile.

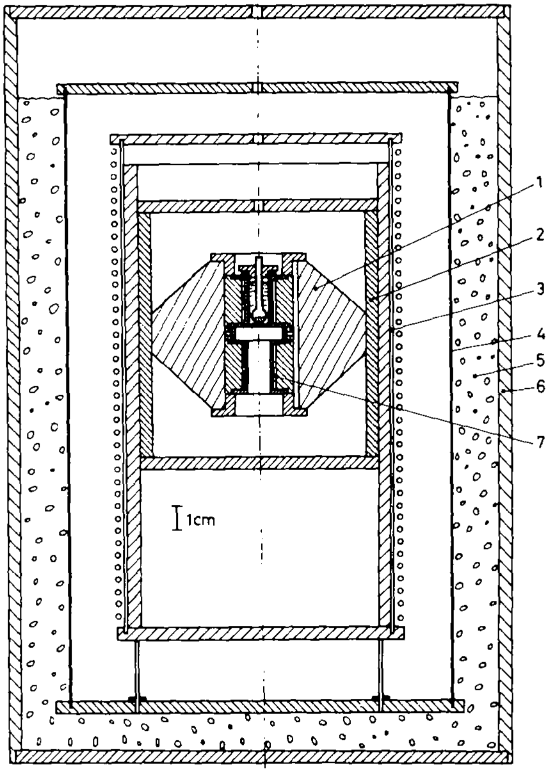

Fig. 1 Cross section in the calorimeter vessel: 1-lens shaped brass block containing the sample and the reference cells along the central axis; 2 - aluminium cavity; 3 - copper shield with the heater and the copper resistor as temperature sensor (non-inductive coils); 4 – stainless steel shield; 5 - rigid polyurethane foam; 6 - Xerox aluminium cylinder; 7 – anodized aluminium cylinder of the reference cell (0.2 mm thick) supporting the copper sensitive coil (approx. 50 Ohm/20 °C)

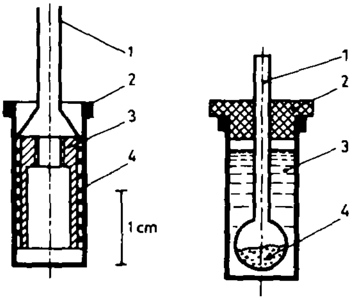

Fig. 2 Sample pan for standard (a) and solubility (b) measurements. a: 1 – coated copper leads (∅ 1.2 mm); 2 – stainless steel pan; 3 - brass core; 4 - NiCr heater coil (∅ 0.15 mm, approx. 16.6 Ohm). b: 1 – glass bubble; 2 – PTFE stopper; 3 – water; 4 – salt

Figure 2 shows cross-sections of two representative sample pans used for standard (a) and solubility (b) measurements. Four stainless steel pans were used, with 0.35 ± 0.01 mm thick walls and a good thermal linkage with the measuring cell.

1.2. *Measuring system*

Figure 3 shows schematically the electric connections used for temperature control and differential measurement of heat flows in the sample and reference cells. For isothermal measurements, a temperature controller (TR) with manual selection of the proportional band (PB) and a threshold sensitivity of 10^{-3} Ohm was used. For temperature selection an external resistive compensation was adapted, with high-precision resistors with metallic films and a helipot (10 KOhm) in parallel connection for fine adjustment in the range of approximately 20–100°. The optimum value of PB has been found by experiments establishing the affine correlation [12, 13] between PB and the resulting lack of balance of the measuring bridge (see section 2 for a similar case). The temperature was read on a digital multimeter with four digits (DM EO302, IEMI, Bucharest) by using a punctiform thermistor (3%/degree) (Th) placed in the brass block.

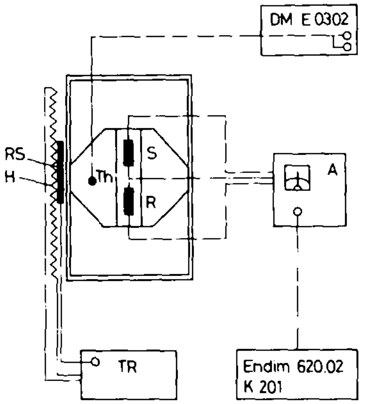

Fig. 3 Electric connections of the calorimetric measuring system and temperature control: digital multimeter (DM EO302), thermistor (Th); ac bridge and lock-in amplifier (A); potentiometer recorder; heater (H) and temperature sensor (RS); temperature controller with manual selection of the proportional band (TR)

The sample (S) and the reference (R) sensitive resistors are symmetrically connected in an ac precision bridge (5 kHz) with a lock-in amplifying system (A). The amplifier output covers the range ± 10 V, but for all sensitivity steps only the range ± 1 V was used. The thermal flows are recorded on two different potentiometric recorders, namely Endim 620.02 (XY-type, VEB–MSW, DDR) and K 201 (Y(t)-type, VEB Carl Zeiss Jena, DDR), corresponding to high and low speed, respectively.

2. Standard measurements

2.1. Calibration

Standard measurements for the calibration of heat flow and overall energy, recorded at different sensitivities in SI units, were made by using a sample pan with an inserted resistor for heat supply, as shown in Fig. 2a. The NiCr heating resistor was normally coiled on the brass core (3) and electrically insulated by two thin layers of adhesive band also making a good thermal linkage with the external pan. Electrical connections for standard measurements are presented in Fig. 4. Heat pulses with constant flow w_p and of duration t_p were realized by simple handling of a two-position switch (S) with double connections. One series of these connections supplies the heating resistor and the other one triggers the digital chronometer with four digits and 1 ms resolution (DC 439, ICEFIZ, Bucharest). The precise values of w_p are obtained by simultaneously measuring on digital gauges the voltage and the current (errors under ±0.5%). The dc generator was built in our laboratory; it was scoped to be free of noise over 0.1%. Thermal flows resulting at standard w_p clearly show two distinct types of behaviour. For short t_p (up to 3 s) and low w_p, the overall flows are composed of two distinct flows (Fig. 5). The deviation from the baseline is expressed in mm, corresponding to 1 mm of recording paper at standard

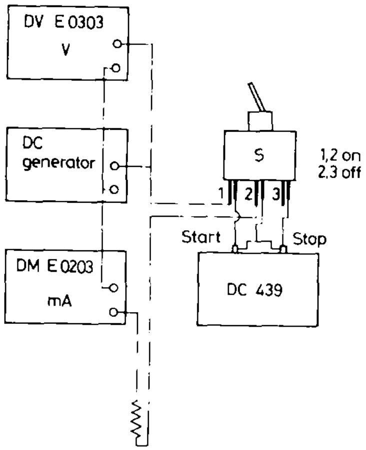

Fig. 4 Electric connections for standard measurements: digital voltmeter (E 0303); digital multimeter (E 0203); digital chronometer (DC 439); two-position switch with double connections (S)

sensitivity: 2×10^3 amplifier sensitivity and 0.1 V/cm on the recorder, or 10^3 and 0.2 V/cm, respectively.

The coexistence of the two thermal flows (w_1, w_2) can be explained by the splitting of w_p between the two capacitive elements C_1 and C_2, respectively, constituting the overall sample pan. In Fig. 6 a detailed cross-section of the measuring system of the sample branch is given. The associated bond digram [7, 16] of the energy circuit expresses the purely dissipative coupling between the two components by element R_1. This bond diagram also corresponds to a simply reacting system [9]. The inner flow source $w_p(t)$ is compensated by the external potential source S at temperature T of the brass block. T_1 is the potential of the pan wall, considered as the response function ($\theta(t) = T - T_1(t)$) for isothermal measurements. The actual measurements were performed at 26.2±0.06°.

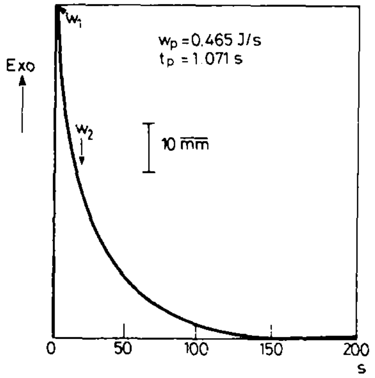

Fig. 5 Typical curve for a standard exotherm obtained by short heat pulse composed by two elementary flows

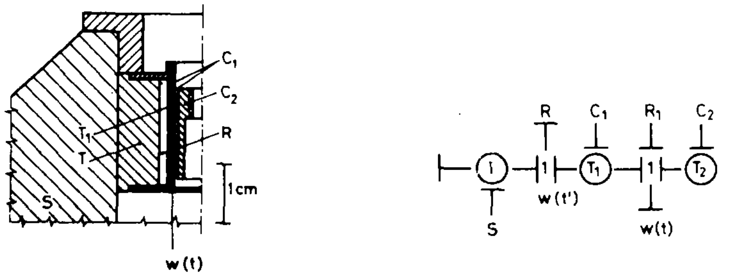

Fig. 6 Identification of capacitive components C_1 and C_2 responsible for the two flows in standard exotherms and the associated bond diagram

For heat pulses with larger t_p and w_p, the recorded flows lose the identity of the constitutive components w_1 and w_2. In Fig. 7 two thermal flows of such kind and different magnitudes are presented at appropriate sensitivities to reveal the same form factor expressed by the ratio peak height (h)/peak are (A).

Flows recorded at a high paper speed allow the determination of some important kinetic parameters. In Fig. 8 three of these parameters are clearly defined on a

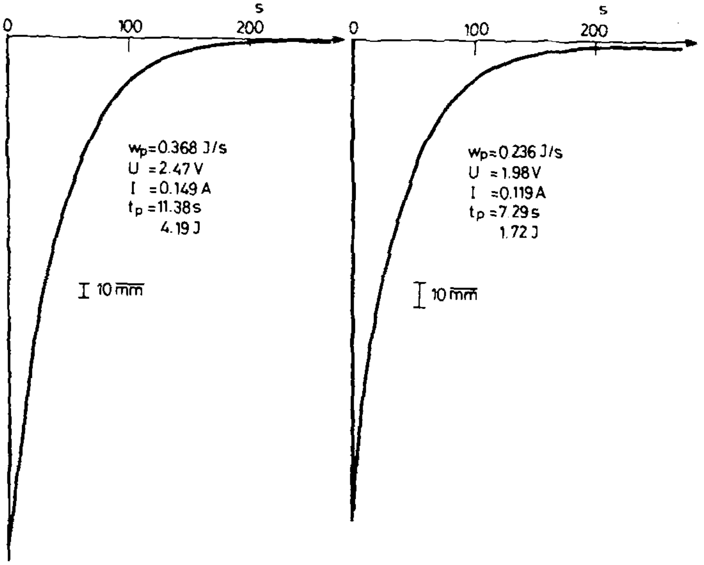

Fig. 7 Two typical standard exotherms obtained for different heat pulses at long t_p times

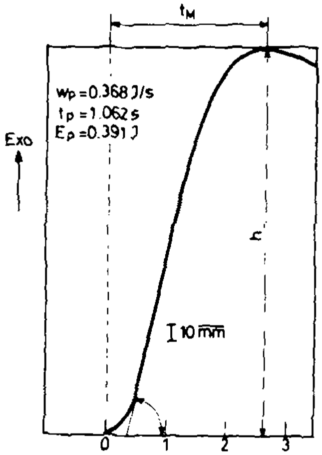

Fig. 8 Standard exotherm of w_1 flow recorded at high speed for which the parameters t_M, τ and h are defined $\tau = (d\theta/dt)_{t=0}^{-1}$

typical standard exotherm with short t_p and low w_p. Up to the peak maximum, this exotherm expresses w_1 flow. It is important to establish the dependence of these parameters as a function of t_p, w_p and the overall energy E_p of the heat pulse.

In Fig. 9 the dependence of the relaxation times $\tau = (d\theta/dt)_{t=0}^{-1} = (dT_1/dt)_{t=0}$ in standard units of s/$\overline{\text{mm}}$ and $(\text{J/s})^{-1}$ are presented as a function of t_p and E_p for different values of w_p. It clearly results that τ attains a saturation value τ_0 for a particular w_p value. By considering τ_0 as a standard value (eigenvalue), from the response function $\theta(t)$ an affine relationship can be verified between (τ_0, w_p) pairs of values, as generally established according to topoenergetic principles [12, 13, 17] (Fig. 10). The optimum PB in the thermal control loop can also be established for this affine correlation. Similar correlations were obtained for h and t_M values in the limits of separated w_1 and w_2 flows.

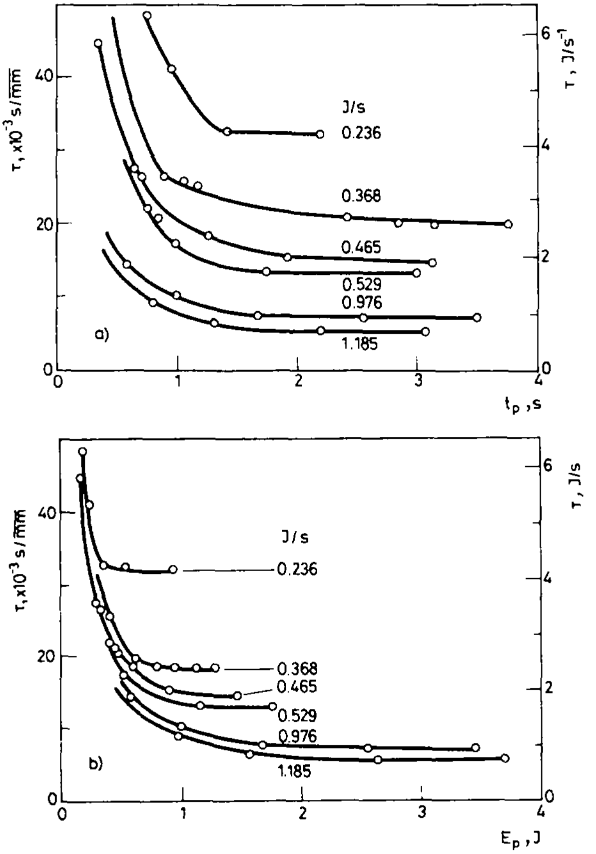

Fig. 9 The dependence of τ for standard exotherms as a function of t_p (a) and as a function of total energy of the pulse, E_p (b), for different amplitude of heat pulse (in J/s)

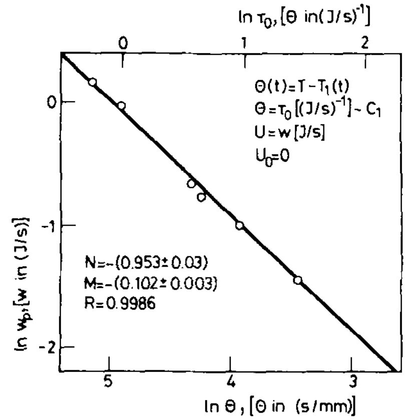

Fig. 10 Affine correlation of saturation τ_0 values and the amplitude of heat pulses

For such standard exotherms, an accurate calibration can be established for parameters h and A in SI units. In Fig. 11 the dependences of $h(t_p)$ and $E_p(t_p)$ for different w_p give a calibration factor of $13.0 \pm 0.2\ \overline{\text{mm}} = 0.1$ J by linear regression. In the same manner, the dependences of $A(t_p)$ and $E_p(t_p)$ give a calibration factor of $(30.8 \pm 0.6)\ \overline{\text{a.u.}} = 0.1$ J. The peak area is measured by planimetry in standard area units, $\overline{\text{a.u.}}$, at the same standard sensitivity and 20 s/cm paper speed. For the K 201 recorder at the same sensitivity, the calibration factor of energy is (14.2 ± 0.3) mm of the integrating band = 0.1 J.

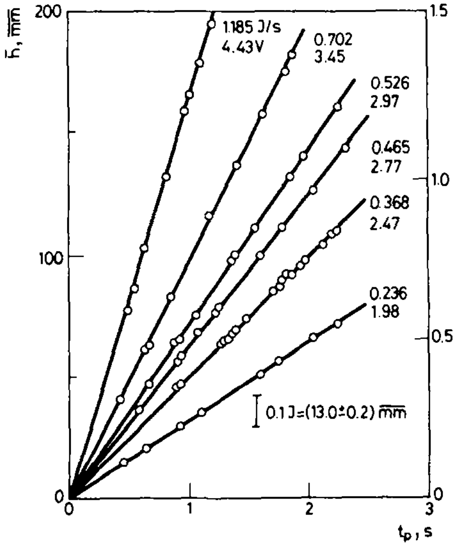

Fig. 11 Dependence of h for standard exotherms as a function of t_p for different amplitude of heat pulses (in J/s and V for the applied electric voltage)

In both graphics, from Fig. 11 we have the linear correlation

$$(h, A) = N_{h,A}t_p + M \tag{1}$$

so that both slope values N have a further linear dependence on w_p:

$$N_{h,A} = n_{h,A}w_p + m, \tag{2}$$

where n are the above-mentioned calibration factors, and $m \simeq 0$.

2.2. *Figure of merit of calorimeter*

It is important to note that $h/A = (0.422 \pm 0.007)\ \overline{\mathrm{mm}}/\overline{\mathrm{a.u.}}$ for all standard exotherms; this ratio represents the figure of merit of the calorimeter as defined for DSC systems [3]. Its exact value is characteristic for a particular inner energy circuit of the transforming (composite) system represented by the equivalent components C_1, C_2 and R_1 [8–10]. Taking these values into account, it successively results that

$$\tau = R_1C_1 \sim 1/h \tag{3}$$

$$A = w_pt_p \sim (C_1 + C_2) \tag{4}$$

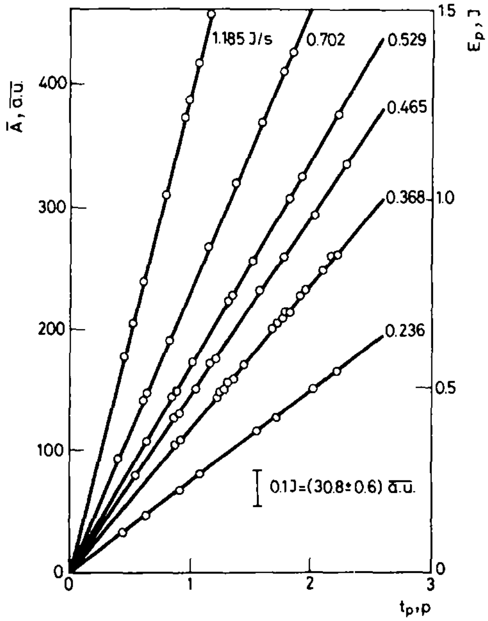

Fig. 12 Dependence of peak area for standard exotherm as a function of E_p for different amplitude of heat pulses (in J/s and V)

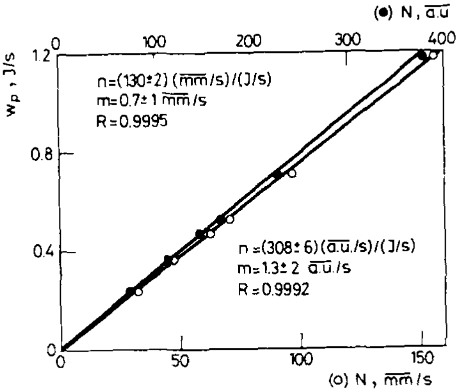

Fig. 13 Linear correlation between slope parameters N associated to $h(E_p)$ and $A(E_p)$ dependences, and the amplitude of heat pulses (in J/s)

so that

$$h/A \sim 1/(\tau A) \sim 1/(\tau w_p) \tag{5}$$

On the other hand, the affine relationship (Fig. 10)

$$\ln \tau_0 = N \ln w_p + M \tag{6}$$

represents a more exact figure of merit, equivalent to h/A (Eq. (5)), because $-N = 0.953 \pm 0.03 \simeq 1$ (but differs statistically from 1).

The affine parameters (N, M) clearly define the nature and the amplitude of the composite system, as recently established for general measuring and composite systems [12, 13, 17]. However, the ratio h/A can be used as an important index of the nature of the transforming system.

It is interesting to mention that a similar result can be obtained by considering the heat pulse as ac perturbation [4, 5]:

$$w_p(t) = w_p^0 \sin \omega t \tag{7}$$

so that the recorded flow becomes

$$w(t) = w_c + w_a(t) \tag{8}$$

where w_c and $w_a = w_a^0 \sin(\omega t + \varphi)$ are the direct and the alternating parts of $w(t)$. From the spectral structure of $w_c(\omega)$ and $w_a(\omega)$, an affine relationship similar to Eq. (6) can be obtained.

3. Concluding remarks

The calorimeter presented in this paper seems to be an appropriate tool for rapid, sensitive and reproducible tests on solubility kinetics under standard experimental conditions imposed by topoenergetic working principles.

The kinetic values of h, t_M, τ and A (or E) expressed in standard units are parameters defined on the overall recorded flow of the triggered transformation process. These values can be considered as eigenvalues and processed according to the universal procedure established on topoenergetic principles [12, 13, 17] with a view to the univocal definition of the nature and the amplitude of the process.

The ratio h/A is an immediate index of the nature of the transformation process.

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Zusammenfassung — Konstruktion, isotherme Betriebsweise (26.2±0.06 °C) und Kalibration eines differentiellen Kalorimeters hoher Leistungsfähigkeit werden beschrieben. Die Konstruktion basiert auf dem Leitfähigkeitsprinzip, wobei Kupferwiderstände benutzt werden, die auf als Temperaturfühler mit sehr geringer Trägheit dienenden Aluminiumzylindern aufgewickelt sind. Zur Messung des Wärmeflusses wird eine Wechselstrombrücke mit einem lock-in Verstärker verwendet. Die Kalibration der Berghöhe (h) und der Bergfläche (A) wird mit kalibrierten Wärmeimpulsen w_p ausgeführt, die mit Fehlern unter 0.5% behaftet sind. Der Wert des Verhältnisses h/A wird für eine große Zahl von w_p-Werten reproduzierbar erhalten, was die Vorzüge des Hochleistungskalorimeters deutlich macht. Dieser Wert ist eine unmittelbare Kenngröße für die Natur des allgemeinen Umwandlungsprozesses. Das kürzlich entwickelte, auf dem topoenergetischen Prinzip beruhende universelle Verfahren wird zur klaren Definition des Prozesses herangezogen.

Резюме Описана конструкция, изотермическое действие 26,2 ± 0,06 и градуировка высокоэффективного дифференциального калориметра. Действие калориметра основано на принципе проводимости медных резисторов, неиндуктивно намотанных на тонкие алюминиевые цилиндры, используемые в качестве температурных датчиков с очень малой инерционностью. Термические потоки измерялись с помощью ас-мостиковой схемы с усилителем. Градуировка высоты (h) и площади (A) регистрируемых пиков проводилась путем использования градуировочных тепловых импульсов w_p с ошибками ниже 0,5%. Воспроизводимое значение отношения h/A получено с большим числом значений w_p, которые являются критерием качества калориметра. Полученное значение является прямым показателем типа общего процесса преобразования. Для определения четко выраженного процесса использован универсальный метод, недавно установленный на топоэнергетических принципах.