

Differential quasi-isothermal microcalorimeter with a digital output

III. Rotational stirring with a continuous rotation rate adjustment

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An electronic apparatus for a differential microcalorimeter is described, enabling continuous operating separately in each calorimetric vessel over a broad range by changing the rotation rate of the step motors in the range 10—700 r.p.m. The results of setting of the zero line, long-term stability at higher stirring intensities, and the plot of values of the energy dissipation by stirring in water at different rotation rates are given.

Описывается электронное устройство дифференциального микрокалориметра, которое дает возможность плавно регулировать мешание отдельно в отдельных калориметрических сосудах в широком диапазоне посредством изменения числа оборотов шаговых двигателей в пределах с 10 до 700 оборотов в минуту. В работе приведены результаты настройки нулевого уровня во времени высшей интенсивности мешания и результаты измерения зависимости величин энергий, вносимых в систему во время мешания, на интенсивности мешания.

An important problem in the measurement of intensively stirred systems in differential calorimeters is attainment of a reasonable slope of the measured value in dependence on time. The accuracy of the measurement using the deflection methods is the greater, the smaller the slope of the recording line obtained and the smaller the differences in the slope value before and after the experiment. Ideal, however experimentally practically unattainable, is the state where the thermal behaviour of the two symmetrical parts of the calorimeter and the thermal input brought into the system by stirring are the same and the resultant thermal effect is eliminated as a result of the differential set up.

In the original experimental arrangement, we employed [1, 2] intense vibration stirring using a vibration stirrer with a controllable vibration amplitude. The zero

slope of the recorded line was attained by appropriately setting the distance of the two stirring arms from the central vibration drive. This method was poorly reproducible and sudden changes in the slope of the recording line often occurred during the experiments as a result of changes in the mechanical part of the stirring device. The fineness of adjusting this regulation was limited by the construction of the vibrator (Vibro Mischer E 1, Chemap A.G., Switzerland), the core of which was not placed at an exactly defined position in the electromagnetic coil.

Therefore we have developed an arrangement which allows continuous operation of the stirrer speed separately in each calorimetric vessel. This arrangement makes possible for appropriate stirring rate adjustment of each stirrer to find conditions under which the thermal input of the stirrers in individual calorimetric vessels and corresponding heat losses from these vessels are comparable, eventually differ in the steady state from constant and acceptable value.

The Z 22 LB 104 step motors [3] were chosen for the drive of stirrers for the following reasons:

- they enable rotation rate regulation over a wide range (1—800 r.p.m.) and the shape of the dependence of the momentum on the rotation rate is satisfactory,
- the electronic solution of the rate regulation using TTL integrated circuits is simple,
- the step motors used have a sufficient power reserve,
- the stability of the rotation rate is given by the stability of the frequency from the control oscillators.

Description of the control unit

Calorimetric vessel and accessories

The twinned calorimetric vessels with a volume of about 200 ml were made of stainless steel (Fig. 1) and placed in a thermostatted block of the calorimeter itself. The temperature detector was made of paired Stantel F 15 MP thermistors (100 k Ω). The heating calibration body was made of a manganin wire spiral with a resistance of ca. 10 and 50 Ω , which was placed in a silica casing filled with transformer oil. A constant current source of 75 and 100 mA was used for powering and was a part of the control unit of the calorimeter.

The system was stirred by a stainless steel three-step stirrer (Fig. 1) constructed so that the stirring in the calorimetric vessel was as intense as possible.

Control of the rotation rate regulation unit

The electronic scheme of the rotation rate regulation unit is outlined in Fig. 2.

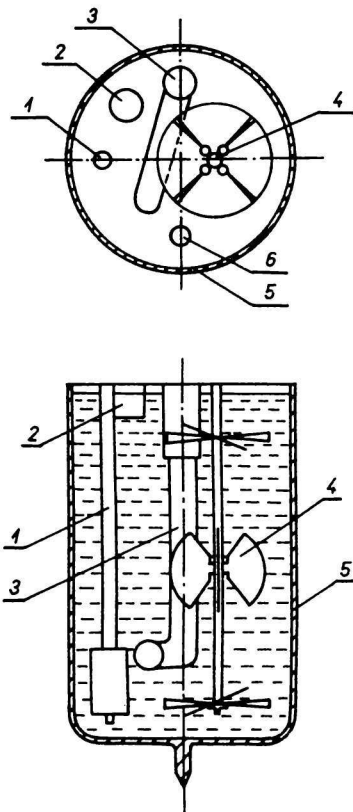


Fig. 1. Vertical and horizontal view on the space distribution of the functional elements in the calorimetric vessels.

1. Ampoule breaker; 2. thermal key enabling the quick equilibration of the inner temperature of the calorimetric vessel with the surrounding block; 3. calibrating heater; 4. three-step stirrer; 5. stainless steel calorimetric vessel; 6. thermistor.

Impulse generator (I)

The generator [4] consists of two MAA 502 operational amplifiers, the first of which acts as an integrator and the second as a comparator with hysteresis. The integration capacitor is temperature-stable with a terylene dielectric. The frequency of impulses is changed using a potentiometer. Both generators are identical and are placed next to one another, which decreases their mutual instability caused by temperature changes.

Impulse frequency divider (II)

The divider consists of MH 7493 TTL circuits. The eight-position switch can be used to adjust the divider ratio from 2 : 1 to 256 : 1.

Commutator (III)

The commutator (III) controls the power keys IV. The individual phases of the step motor V are gradually connected, which here involves a four-stroke control system. The commutator also consists of TTL circuits.

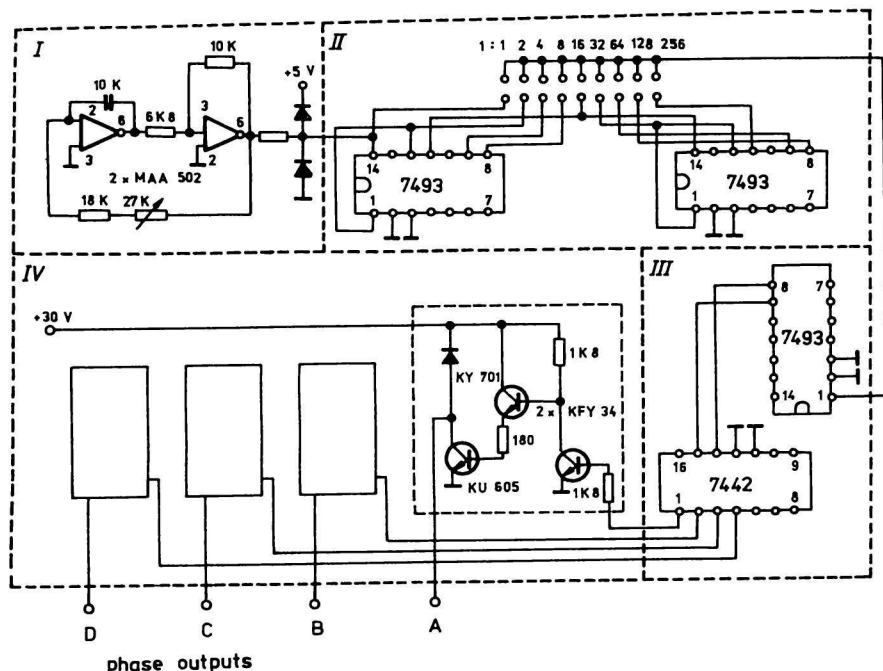


Fig. 2. Circuits for the impulse generator, impulse frequency divider, commutator, and power keys.

Power keys (IV)

The power keys consist of common silicon transistors of the KU 605 type. The diodes are protective elements for power keys (an induction load).

The described electronic unit enables the continuous rotation rate regulation of both motors in the range 10 to 700 r.p.m. Both motors can be controlled only by a single generator (I) as well, so that the two stirrers work synchronously. If the slope of the recorded line at given stirring intensity is too steep, then this synchronous adjustment can be changed for the separate rotation rate control for each motor, which has to be so precise that comparable steady thermal flows between both vessels and surrounding environment can be attained and the slope of the recorded line becomes to be acceptable for recorded line analysis with relatively better accuracy.

Experimental and results

Intensity of stirring and quality of the recorded line

All systems, especially those involving mixing of two difficult miscible phases should be carried out with as intense stirring as possible during the measurements. An increase in the

stirring intensity by measurements in the differential calorimeters leads to enlarged values of the recording line slope, as there are large differences in the dissipated energy introduced into the system by the stirrers. Slow stirring, on the other hand, results not only in insufficiently rapid mixing of the reacting components, but in a thermal inhomogeneity of the measured systems, leading to the recorded line scattering. Therefore, the thermistors are usually provided with a capacity components in calorimetric devices (metallic extensions, submersion of the thermistor bead in mercury, electronic signal damping), which plays the function of the integrating unit. In our case, where the relative high mixing efficiency is desirable, we are always using the undamped thermistors. We have found that an increase in the intensity of the stirring led to a smoother recording line and that the noise level decreased for the recording range of the whole recording by 6.1 J (Table 1).

Table 1

Dependence of the noise level on the stirring intensity

Revolution rate r.p.m.	Maximum spread of the noise scatter J
47	$\pm 12.2 \times 10^{-2}$
91	$\pm 7.7 \times 10^{-2}$
184	$\pm 6.1 \times 10^{-2}$
381 and higher	$\pm 4.6 \times 10^{-2}$

It is apparent from the presented data that a satisfactory recording line with undamped thermistors has been attained at a stirring intensity of >100 r.p.m. where the thermal inhomogeneity of the system is of an acceptable value.

At higher stirring rates, however, differences in the efficiency of the stirrers appeared, which results in dissipated energy differences incorporated into systems by stirrers and the slope of the recording line becomes to differ from zero. In Table 2 are presented the experimentally found differences in the dissipated energy between the two stirrers for different stirring intensities in water under condition that both stirrers are working at identical stirring rates in both calorimetric vessels.

Table 2

Experimentally determined differences in energies
incorporated into calorimetric vessels by stirrers
in dependence on stirring intensities

Revolution rate r.p.m.	Differences in dissipated energies between stirrers J min^{-1}
100	6.5×10^{-2}
298	14.6×10^{-2}
607	83.3×10^{-2}

Straightening of the recording line through a revolution rate change of stirrers

It follows from the preceding part that it would be possible to attain almost zero slope of the recorded line just by an appropriate change of the stirring rate in one of the calorimetric vessels. The experiments in which the solid phase should be fluidized must be carried out under intense stirring and the electric calibration before and after the experiments should be performed under the same experimental conditions. At higher stirring intensities, however, the distinct differences become to appear in symmetry of both differentially connected calorimetric units and the recording line assumes an unacceptable steep course. The calibration experiments can be thus evaluated with an appreciable uncertainty due to the deteriorated signal—noise ratio.

For example in the experiment where the stirring in the both calorimetric vessels was the same, 607 r.p.m., the recording line deviated from the zero line by $\sim 0.8 \text{ J min}^{-1}$ (Table 2). Decreasing of the intensity of stirring of one of the stirrers to 504 r.p.m. led to a good straightening of the recording line slope and the deviation from the zero line made $9.8 \times 10^{-3} \text{ J min}^{-1}$ (Fig. 3A). This slope of the recorded line got settled practically immediately after stirring rate adjustment and retained unchanged during 1 h.

The results of the evaluation of eight measurements of the calibration heats for stirring rates in both calorimetric vessels of 607 r.p.m. and for the case of recorded line straightening by the rate change in one of the calorimetric vessels by

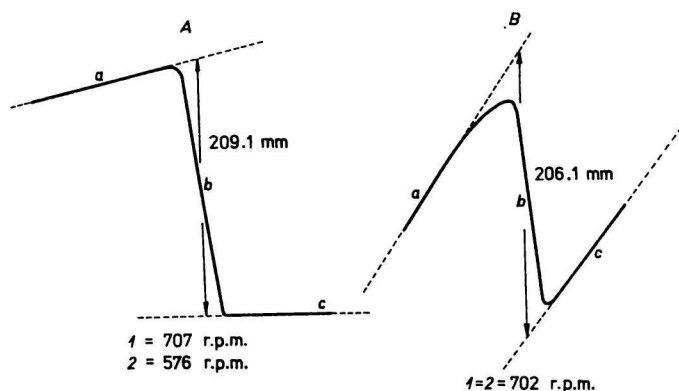


Fig. 3. Recorded lines of the calibration experiments for the same and corrected stirring rates.

1, 2. Stirring rates in the calorimetric vessels 1 and 2.

a), c) Recorded line before and after the calibration; b) recorded line during the calibration.

A. Calibration experiment under corrected stirring rates; B. calibration experiment at the same mixing rates in both calorimetric vessels.

~103 r.p.m., led to the following conclusions. The mean value of the calibration heat calculated from the recording lines with a great deviation from the zero line was of about 1.5% lower with an experimental scatter of $\pm 1.7\%$, than the mean value of the calibration heat with the results scatter of $\pm 0.2\%$ as calculated from the straightened recording line.

Measurement of the energy dissipated by stirring

The experimental apparatus described enables also the determination of the dissipated energy introduced into system by the individual stirrers.

The measurement of the dissipated energies was started by recording the line of a thermally balanced calorimetric system in nonagitated state. The slope of the recorded line was always practically equal to zero under these conditions. Subsequently, the mixing in one of the both calorimetric vessels was started at given mixing rate and continued until the steady state was reached, when the slope of the recorded line became constant. The calibration experiment was performed in the same calorimetric vessel and at the same mixing intensity but by mixing in both calorimetric vessels; the electric calibration made it possible to calculate the value of the dissipated energy of the given stirrer in the given calorimetric vessel for studied mixing rate.

In Fig. 4 the dependence of the energy dissipated by stirring on the stirring intensity over the range 100—700 r.p.m. is given. The dependence is roughly cubic, corresponding to the common empirical correlations (stirring intensity — dissipated energy) and can be written in the following forms for both stirrers (curves 1

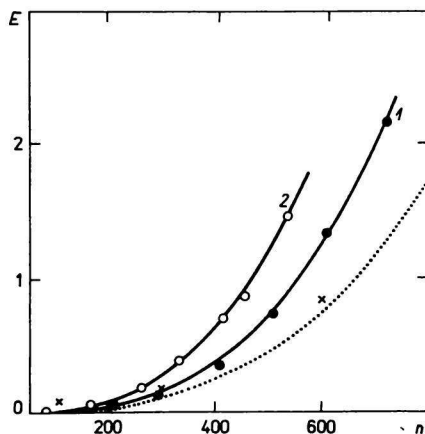


Fig. 4. Dependence of the dissipated energy on the stirring intensity and the comparison of directly measured and calculated differences in energies dissipated by individual stirrers.

1, 2. Stirrers in the calorimetric vessels 1 and 2.
 E — Dissipated energy incorporated into systems by stirring, J/min; n — r.p.m.; dotted curve — calculated differences $E_2 - E_1$ from the empirical equations; \times — measured differences in dissipated energies (Table 2).

and 2 in Fig. 4 correspond to the stirrers in the calorimetric vessels 1 and 2)

$$E_1 = 5.147 \times 10^{-9} n^{3.016}$$

$$E_2 = 1.776 \times 10^{-8} n^{2.897}$$

where n is the number of revolutions per min and energy E is in J min^{-1} .

In Fig. 4, the comparison of directly measured and calculated differences of dissipated energies incorporated into systems by stirring in dependence of stirring intensities is also illustrated. The dotted curve shows the $E_2 - E_1$ differences according to the equations mentioned above; points are experimentally determined differences (Table 2). The comparison of the calculated and measured differences can be taken as a satisfying consistency test of the measured data.

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