Differential quasi-isothermal microcalorimeter with a digital output. I. Electronic control unit

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The control unit of a differential quasi-isothermal microcalorimeter of the Dewar type with a direct current bridge, comprising a time unit, current sources, and the output to a digital voltmeter is described. The results of calibration on the heat of solution of potassium chloride in water and the reaction heat of tris(hydroxymethyl)aminomethane in 0.1 N-HCl at 25°C are presented.

В работе дано описание блока управления дифференциального, псевдо-изотермического микрокалориметра типа Дьюара с мостиком на постоянном напряжении, с собственным блоком времени, источником питания и выходом на цифровой вольтметр. Приводятся результаты калибровки по теплоте растворения хлористого калия в воде и определения теплоты реакции трис(гидроксиметил)ами-нометана в 0,1-н HCl при 25°C.

After several years of experiments with the differential quasi-isothermal microcalorimeter with an alternative current bridge [1] we found out some imperfections limiting the accuracy of measurements (inaccurate measurement of time, difficulties in the determination of the values of calibrating heatings at short heating intervals, difficulties in linking up with the digital processing of the measured data). These were the reasons which led us to designing a new electronic control unit for the calorimeter.

We applied a direct current bridge as there were available commercially produced stable low-noise operation amplifiers with a small thermal drift. This simplified substantially the construction as well as the feeding of the bridge, and made a direct transmission of the signal from the amplifier to the recorder and digital voltmeter possible. The application of the direct current bridges for the calorimetric purposes is quite usual and it is frequently preferred to the alternative current feeding [2, 3]. However, we are aware of the fact that the suitability of the both types of bridges can be considered from different aspects, mainly with respect to the applied criteria [4].

For a precise measurement of time an independent time unit was built into electronic control unit from which the sampling of the output signal from the digital voltmeter into the converter was derived. This solution allows a direct transfer of the signal on a punched tape and a subsequent processing of the experimental results by a computer. Stabilized current sources were built into the control unit in order to attain an exact determination of the calibrating heats.

The mechanical part, except for some minor rearrangements, was the same as in our previous work [1].

Description of the calorimeter

Calorimetric vessels and accessories

Twinned calorimetric vessels of a Dewar type with a content of *ca.* 300 ml were mixed by vibration and immersed in a thermostated water bath (25 ± 0.002°C). As thermal detectors thermistors with an increased heat capacity (the bead of the
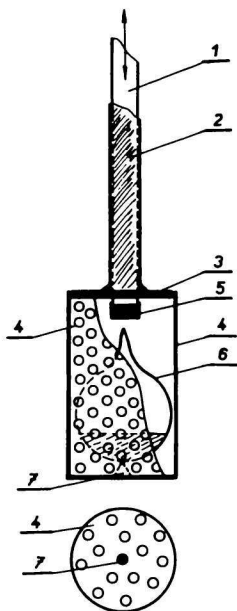

Fig. 1. Crushing device.

1. Sliding plexiglass rod; *2.* metal holding tube hold in a teflon stopper in the cover of the calorimetric vessel; *3.* supporting plate; *4.* perforated vessel screwed to the supporting plate; *5.* stainless jacket of the sliding rod; *6.* glass ampule with the sample; *7.* stainless mandrel.

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thermistors was covered by a protecting shell) were used. As compared to the original design [1], the construction of the calibrating heating and of the opening device has been changed.

The original opening device with an excentrically suspended overturning vessel was found to be unsuitable since frequently the sample was not transferred quantitatively into the reaction area. Therefore the sample was sealed in a thin-walled glass ampule which was crushed by the pressure of a stem in the crusher (Fig. 1). The heat effect of this operation amounted to an average value of 0.084 J.

The platinum calibrating heating was replaced by the manganine heating ($d = 0.15$ mm, *ca.* 10 Ω) allowing to work with both quick and slow thermal response. In the former case the insulated spiral-shaped manganine wire was covered by the resin Delta Bond Kit 152-K-A (Wakefield Eng., Wakefield, Mass., USA) with a good thermal conductivity and a high electroinsulating ability. In the latter case, the manganine spiral was immersed in a small quantity of the transformer oil contained in a quartz ampule.

The electronic control unit

The block scheme of the electronic part of the control unit is shown in Fig. 2. The output signal of the disbalanced bridge is led to an amplifier with the possibility of a gradual amplification. The amplified signal is recorded by a recorder EZ 11 and simultaneously processed by the digital voltmeter, the converter, and punched into a tape. The time unit includes a quartz crystal oscillator and a counter with
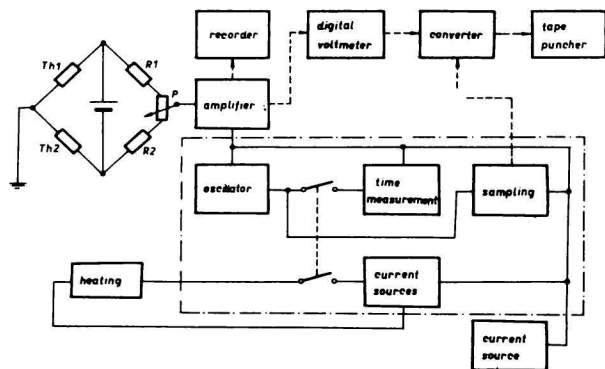

Fig. 2. Block scheme of the calorimeter control unit.
Th1, Th2 — coupled 100 k thermistors Stantel F15MP; *R1, R2* — 100 k; *P* — Aripot 1 k.

a digitron display for time measurement. The starting pulse for the transmitters is derived from the clock pulses of the oscillator. The calibrating heating and other blocks of the control unit are fed by the direct current sources.

Bridge and amplifier

The circuit scheme of the bridge and amplifier is shown in Fig. 3. The bridge consists of the coupled 100 kΩ thermistors Stantel F 15 MP (Standard Telephones and Cables Ltd., Footscray, Sidcup, Kent, England) connected to the connectors *TH1*, *TH2*, a couple of thermally stable 100 kΩ resistances *R12*, *R13* and a potentiometer *P1* (Aripot, 1 kΩ, 10 rev.), and it is fed by a Ni—Cd battery B —1.2 V connected in a series with a compensation unit *K* (thermal compensation). The battery can be charged from the charging source + 24 V. The thermal coefficient of the used thermistors $\alpha = -4.7\%/°C$ at 20°C.

The current evaluation of the disbalancing of the bridge is carried out in connection with the operational amplifier *A1* [5]. The feedback resistance of the amplifier consists of a *T* element (resistances *R1, R2, R3, R4, R5, R6*). By means of the switch *PR1* it is possible to change the gain of the amplifier *A1* in steps denoted in the scheme as *1, 2, 5, 10*. To the output of the amplifier *A1* the second
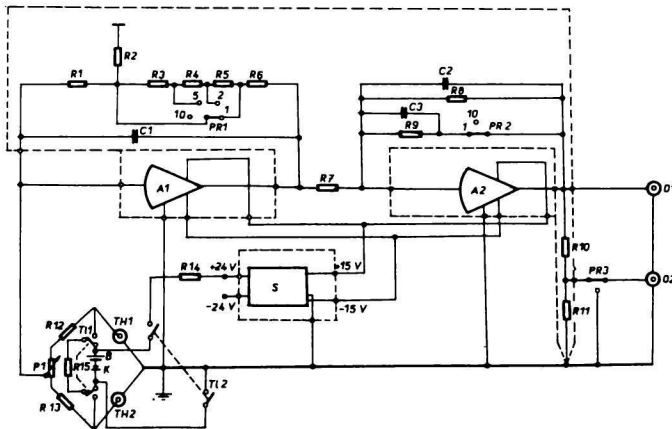

Fig. 3. Bridge and amplifier.

R1 — 100 k; *R2* — 100; *R3* — 24 k; *R4* — 15 k; *R5* — 5 k 1; *R6* — 5 k 1; *R7* — 10 k; *R8* — 1M; *R9* — 120 k; *R10* — 100 k; *R11* — 100; *R12* — 100 k; *R13* — 100 k; *R14* — 120; *R15* — 100 k; *C1* — M1; *C2* — 2M; *C3* — 8M; *P1* — 1 k; *B*—Ni—Cd battery; *TH1, TH2* — input for the 100 k thermistors; *K* — compensating unit; *S* — double stabilized source AS901; *A1, A2* — operational amplifier AS101; *01, 02* — outputs; *Tl 1* — push button for the bridge feeding connection; *Tl 2* — battery charging push button; *PR1* — gain switch A1; *PR2* — gain switch A2; *PR3* — output *02* switch.

stage *A2* is connected. In the second stage *A2* it is possible to select the gain *1* or *10* by means of the switch *PR2*. The amplifier has two outputs: *01* for the digital voltmeter and *02* for the recorder. In the construction of the amplifier two operational amplifiers of the type AS101A and a feeding source of the type AS901 were used. The final thermal stability of the amplifier is better than 1.1 µV/°C and the noise level with respect to the input voltage at the maximum gain is 6 µV.

Time unit

The wiring diagram of the time unit is shown in Fig. 4. The time unit allows a precise measurement of the duration of the calibrating heating in the calorimetric vessels and the sampling of the output signal from the digital voltmeter to the converter. The basis of the time unit is a crystal-controlled 10 kHz oscillator, which consists of two operational amplifiers *A1*, *A2* of the type MAA502, crystal *CR*, and another circuits. The positive feedback is led from the output of the operational amplifier *A2* through the series resonance impedance of the crystal *CR* to the non-inverting input.

The amplitude of the output potential from the oscillator is stabilized by
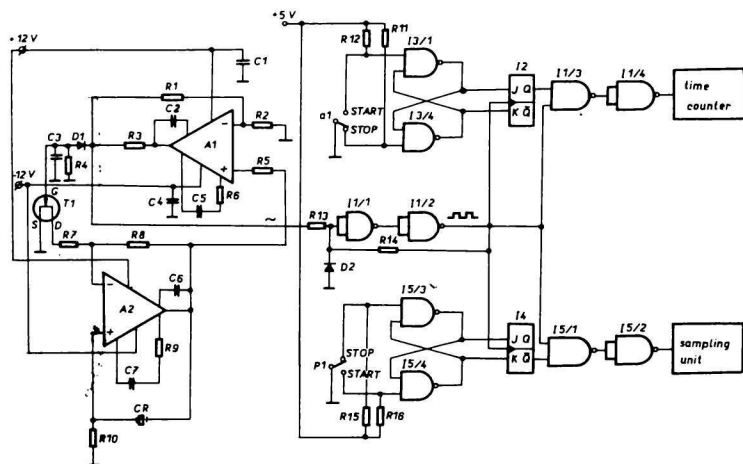

Fig. 4. Time unit.

R1 — 27 k; *R2* — 1 k; *R3* — 56; *R4* — 1M; *R5* — 1 k; *R6* — 1 k 5; *R7* —5 k 1; *R8* — 20 k; *R9* — 8 k 2; *R10* — 5 k 1; *R11* — 4 k 7; *R12* — 4 k 7; *R13* — 3 k; *R14* — 2 k 2; *R15* — 4 k 7; *R16* — 4 k 7; *C1* — M1; *C2* — 22; *C3* — 47 k; *C4* — M1; *C5* — 470; *C6* — 100; *C7* — 4 k 7; *A1, A2* — MAA502; *T1* — 2N3819; *D1,2* — KA206; *CR* — crystal 10 kHz; *I1* — MHA111; *I2* — MJA111; *I3* — MHA111; *I4* — MJA111; *I5* — MHA111; *P1* — sampling start switch; *a1* — relay contact for the time measuring switch on.

a feedback leading to the inverting input $A2$ through the separator $R8$ and $R7$ in a series with the resistance of the DS path of the "FE" transistor $T1$. The output alternating voltage is led from $A2$ through the separating element $A1$, rectified by the diode $D1$, filtered by $C3$ and brought to the electrode G of the transistor $T1$. The stabilization loop of the amplitude of the exit voltage works in such a way that, *e.g.* with increasing alternating voltage at the output $A1$, the potential of the electrode G of the transistor $T1$ increases, thus increasing the resistance of the DS path as well as the resistance of the feedback in the circuit $A2$, and decreasing the amplitude on the output $A2$. The stability of the frequency of the oscillator is 1×10^{-4}

The sinusoid signal from the output $A1$ of the crystal-controlled oscillator is rectangularly shaped by means of a Schmitt's circuit consisting of the gates I-$1/1$, I-$1/2$ and resistances $R13$ and $R14$. The diode $D2$ protects the input of the gate against the negative potential. The shaped signal is led to the controlled input of the time measuring counter (measurement of the duration of heating) and of the sampling unit. The counter allows to measure time in the range from 10^{-3} to 10^3 s with an accuracy of 10^{-3} s. The measurement of time is started by means of the contact $a1$ synchronically with the switching on a stabilized current source for the calibrating heating. The sampling unit consists of a series of frequency dividers. The converter is started by an impulse with the amplitude of 2.4 V, the interval being optional 0.5, 1, 2, 4 or 8 s.

Current sources

The scheme of connection of the current source is shown in Fig. 5. The connection of a constant current source with an ungrounded load [6] connected to the output clamps *1, 2* was used. The high output impedance of the source was achieved by insertion of a parallel current feedback from the reference resistance $R11$ through the resistance $R6$ to the inverting input of the operational amplifier A. Zener's diode D connected through the resistance $R2$ to the inverting input of
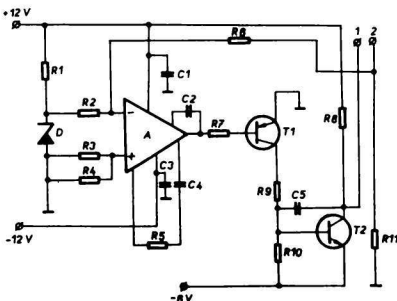

Fig. 5. Current sources.
$R1$ — 820; $R2$ — 6 k 2; $R3$ — 6 k 2; $R4$ — 200 (for 100 mA); 150 (for 75 mA); $R5$ — 8 k 2; $R6$ — 200 (for 100 mA); 150 (for 75 mA); $R7$ — 2 k; $R8$ — 10 k; $R9$ — 1 k; $R10$ — 470; $R11$ — 2 j 7; $C1$ — M1; $C2$ — 220; $C3$ — M1; $C4$ — 4 k 7; $C5$ — 1 M; D — 1N2624; A — MAA502; $T1$ — KF517; $T2$ — KF508; *1., 2.* — clamps for the calibrating heating.

the operational amplifier serves as a source of the reference voltage. The output stage of the source is formed by a connection of complementary transistors *T1, T2*. The control unit contains two independent stabilized current sources 75 and 100 mA. The stability of the current is better than $1^o/_{oo}$. Prior to the measurement, both sources are loaded by a standard resistance of 10 Ω (the resistance of the calibrating heating is about of the same value) and the selected source is switched to the calibrating heating in the calorimetric vessel only for the actual calibrating measurement.

The feeding source

The feeding source of the control unit consists of standard transistor stabilized voltage sources $+5$, -6, ± 12 and ± 24 V [7] which feed different parts of the apparatus, and of an unstabilized source $+250$ V for digitrons anodes.

Results of calibrating measurements

The operation of the calorimeter was tested by measuring the heat of solution of potassium chloride (Merck-Suprapur) and the reaction heat of tris(hydroxymethyl)aminomethane — THAM (K&K Laboratories Inc., Plainview, N.Y.). The reaction and the calibrating heats were determined graphically on the basis of the course of the measured curves.

The average value of the heat of solution of potassium chloride at 25 °C for the weighed-in amounts of 40—80 mg and a molar ratio $KCl:H_2O = 1:13\ 500—25\ 000$ for eight measurements, corresponds to the value 17 309 with an estimated error of ± 29 J mol^{-1}

The average value of the reaction heat of tris(hydroxymethyl)aminomethane at 25°C for the weighed-in amounts of 80—112 mg in 220 ml 0.1 N-HCl for eight measurements corresponds to the value 29 836 with an estimated error of ± 50 J mol^{-1}.

The determined value of the heat of solution of potassium chloride lies within the range of values presented by other authors [8]; it is somewhat higher than the value $17\ 196 \pm 209$ J mol^{-1} determined in our previous work [1] and it is close to the value presented by *Lange* and *Mönheim* [9] at 25°C and extrapolated for the investigated range of dilution and the dependence of the heat of solution of KCl upon the dilution (17 322 J mol^{-1}). The determined inferior limit of the heat of reaction of THAM in 0.1 N-HCl (29 786 J mol^{-1}) is in a good agreement with the data presented by *Prosen* and *Kilday* (29 769 J mol^{-1}) [10].

Conclusion

The results obtained with the proposed control unit of the calorimeter were found to be fairly good. The proper time unit and the current sources simplified both operation and the calibrating experiments. The reproducibility of individual measurements is superior to that achieved with the previous device [1]. The output on the punched tape through the digital voltmeter, converter, and the tape puncher, as well as the processing of results will be dealt with in the subsequent communication.

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