ISOTHERMAL CALORIMETER FOR MEASURING ENDOTHERMIC HEATS OF MIXING*

F.Veselý, V.Hynek, V.Svoboda and R.Holub

*Department of Physical Chemistry,
Institute of Chemical Technology, 166 28 Prague 6*

The design of an isothermal mixing calorimeter and its measuring and control parts are described. The calorimeter was tested by measuring the heats of mixing in the following systems: methanol––benzene at 25 and 45°C, benzene–cyclohexane at 50°C and tetrachloromethane–benzene at 25°C. The concentration dependence of the heats of mixing was correlated for all systems by expansions of the Redlich–Kister type. A comparison of the measured excess enthalpies with selected literature data, which may be considered as reliable, confirms that the plausible experimental error is $0.3-0.5\%$ for the heats greater than 400 J mol^{-1} and the maximum error is 1% for values below 100 J mol^{-1}.

A rapid development of mixing calorimetry has been recently observed, brought about by elaborating the theories of liquid solutions by the statistical thermodynamics methods and, simultaneously, by progress in electronic devices which made it possible to achieve high experimental accuracy. This usually determines general features of studies on heats of mixing which are aimed either at verification of theoretical conclusions and finding new interpretations of the mixing process or at improving the experimental technique.

   This communication belongs to the last of the enumerated groups and it encompasses results of work performed with the aim of constructing such a calorimeter, that the total mixing process approach maximally the isothermal course. The conception of the calorimeter has been based (as that of several recently developed isothermal devices) on an accurate determination of amounts of mixed liquids and a measurement of electrical energy necessary for maintaining isothermal conditions. This eliminates the otherwise unavoidable determinations of both time changes in the temperature, which is very laborious and little accurate at the same time, and the heat capacity of the calorimeter. As the determination of the amounts of mixed liquids and the electrical energy delivered is comparably least difficult of possible methods of measuring necessary quantities, it was plausible to assume that this arrangement would at present yield the possibility of obtaining relatively highest accuracy.

EXPERIMENTAL

Calorimeter

The calorimeter is composed of a mixing vessel, a proportionally controlled (adiabatic) jacket, an external thermostat and a protecting aluminium jacket.

Mixing vessel (Fig. 1) is of cylindrical shape of diameter of 30 mm and height 80 mm. It is made of brass. A brass 13 mm-long annulus 1 provided by a thread on its inner perimeter is soldered into the central part of the vessel. Its lower part diminishes the diameter of the vessel to 23 mm and it serves for fixing the aluminium membrane 2 between teflon packings 3. Perfect tightness between them is secured by a screwed-in brass ring 4. The lid of vessel 5 is provided by a filling hole closed by screw 6 with teflon packing 7. The lid and the widened upper part 8 of the vessel posses a hexagonal profile and they are connected by a thread. A simple original device for breaking the aluminium foil is fixed to the inner part of the lid. It consists of metal drift 9 of a conical shape bored axially by six holes (diameter 4 mm) connecting the two compartments in the case of the drift sticking in the membrane. Steel spring 11 is mounted on guiding rod 10. The spring is compressed after inserting the rod into groove 12 and then fixed in this position by lock 13 on holder 14. A rotation of the calorimeter by $90-130°$ and several slight knocks on the calorimeter jacket at the height of the lid of the mixing vessel are sufficient for loosing the spring and shooting the drift. This produces a slight displacement of the massive holder 14 from its equilibrium position, which suffices for removing lock 13 by spring 15. The lower part of the vessel is provided by a second filling hole 16, closed again by a screw with the teflon packing. A teflon cylinder 18 is attached to the bottom of the vessel by three screws 17. Copper leads 19 of resistance thermometers and a heating are drawn through its circumferential part. Two resistance platinum thermometers ($\sim 100\Omega$, diameter 0·05 mm) and a manganine heating (145Ω, diameter 0·1 mm) are wound bifilarly on jacket 20 of the mixing vessel. Both the jacket of the vessel and the coiling were mutually insulated by subsequent laminating and polymerization of an electroinsulating varnish.

Adiabatic jacket. It is an aluminium cylinder of the inner diameter of 120 mm, wall thickness 12 mm and height 140 mm, with its surface provided by several layers of the insulating varnish and two platinum resistance thermometers (100Ω, diameter 0·05 or 0·1 mm, resp.) and manganine heating (185Ω) coilings. Three teflon bushings for electrical connections between the mixing vessel and remaining parts of the calorimeter are pressed in the three holes in the bottom of the jacket. Four cylindrical polyamide legs are located between the bottom of the adiabatic vessel and the external thermostat. This space contains manganine resistances of the Wheatstone bridge (*cf.* below).

External thermostat is also an aluminium cylinder (inner diameter 180 mm, height 200 mm, wall thickness 5 mm) with its surface coated by three layers of the electroinsulating varnish and bifilarly wound platinum resistance thermometers (100Ω, diameter 0·1 mm) and kanthal wire heating (275Ω) coilings. Teflon bushings for the outlet of all internal connections are pressed in the thermostating jacket near the rotation axis. The complete calorimeter is suspended in a massive stand on bearings screwed to both sides of the jacket. The calorimeter may be rotated manually by a handle in both directions by 180°. The outer surface of the calorimeter is formed by a protecting aluminium jacket (wall thickness 1 mm) with a bottom and a lid which may be dismantled and which are attached to the external thermostat.

Measuring and Control System

For the temperature control, a similar controlling system was used as in the evaporation calorimeter[1]. A series of changes was, however, performed, aiming at an easier and quicker manipulation with the device, an increased reliability of the circuitry and decreased dimensions and weight of the control units. An easier manipulation was brought about by an automatic temperature control of the external thermostat by the temperature of the adiabatic jacket (drat control, *cf.* Fig. 2). The additive circuit of the third control channel (Wheatstone bridge) is fixed so that the automatic controller R_3 may maintain the temperature of the external jacket (system S_3 by $1 \cdot 5 - 2 \cdot 0°C$ lower than the temperature of the adiabatic jacket. Temperature control circuits of the mixing vessel, which are the same as in the evaporation vessel of the evaporation calorimeter, were also described earlier[1]. The d.c. power stage of the temperature control of the adiabatic jacket (second control channel) was replaced by an a.c. thyristor control. The signal from the synchronized detector is added to the saw tooth voltage of the frequency of 50 Hz. This voltage is transformed by the Schmitt circuit into pulses of a changing width, which switch on a multivibrator vibrating at a frequency of $\sim$3 kHz. This a.c. voltage (bundles of pulses) controls the thyristor *via* an isolating transformer. The zero control deviation of the second control channel is adjustable for $(T_1 - T_2)$
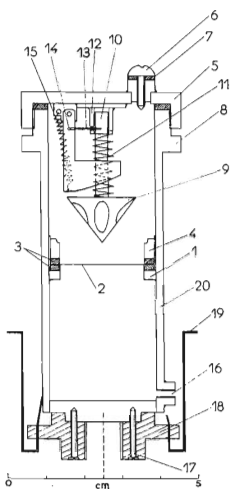

FIG. 1

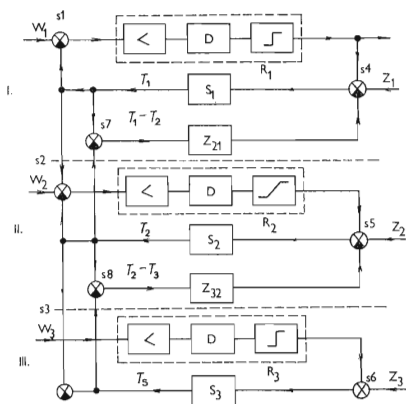Mixing Vessel
  For the description *cf.* the text.

FIG. 2

Block Diagram of the Calorimeter
  For the description *cf.* the text.

in the range $0-0.1°C$ (*cf.* Fig. 2, W adjusting of the temperature run). The same circuits as in the second control channel were used for the third control channel. The single difference is in adjusting the control deviation which is zero for $T_2 - T_3 = 1.5-2.0°C$. The most significant changes in the design are the unification of the circuitry into units possibly interchangeable for all control channels and a changed arrangement of the operating elements on the front panel of the control unit. A detailed description including diagrams of all circuits is given in a research report[2].

Preparation of Pure Components

The following systems were chosen for testing the calorimeter: methanol–benzene at 25 and 45°C (with respect to a plan of measuring the temperature dependence of approximately equally large excess enthalpies in mixtures of similar properties), benzene–cyclohexane at 50°C, and tetrachloromethane–benzene at 25°C (it has been studied many times and, moreover, small heats of mixing and a large difference in the densities of both components make it well possible to verify the quality of the mixing process). Methanol, benzene and cyclohexane were purified by the same methods and with the same resulting values of the physicochemical constants as in a previous work[1]. Tetrachloromethane, AR grade, was dried by anhydrous copper sulphate and calcium chloride and then four times distilled on a packed column of a $\sim$30 TP efficiency and with the reflux ratio of 40 : 1. The resulting physical constants of the final product were n_D^{25} 1.4575 (ref.[3] 1.4576), d_4^{25} 1.584444 (ref.[3] 1.58445) and the n.b.p. 76.78°C (ref.[3] 76.75). The impurity content determined mass-spectrometrically was less than 0.1%.

Measuring Procedure

Filling of the mixing vessel. Several mutually connected polyethylene bags (volume of each of them $\sim$0.15 cm^3) were placed along the circumference of the lower half of the vessel to make up for volume changes of liquids (thermal expansion, volume of mixing) and to eliminate the vapour phase. The lower part of the vessel was closed by the aluminium foil, the same number of the bags was placed into the upper half and then the lid with the attached drift was screwed in. Both parts of the vessel were subsequently filled with syringes. To mix pure components in other ratios than those corresponding to the original volumes, the volume of the lower part of the vessel was adjusted by glass beads. For limiting concentration values, a mixture of known composition was diluted by one or other pure component and the excess enthalpy was calculated from the measured heat of dilution. The amounts of substances were determined from differences in the masses of the syringes before and after filling. The filled mixing vessel was attached to the bottom of the adiabatic jacket and corresponding wires were soldered to the thermometers and heating terminals. As the polyethylene bags were often bursting at 45 and 50°C due to a relatively low melting point of the polymer, we left a vapour space over the liquids instead. In accordance with Lundberg's measurements[4] we chose an 1/10 of the liquid phase as an optimum, *i.e.* 2 cm^3 for each component.

Measurements. The time necessary for reaching the required temperature in the water after switching on the automatic temperature control fo the vessel, the adiabatic jacket and the external thermostat ranged from several minutes (at 25°C) to one hour (50°C). The "course" of the calorimeter, *i.e.* a constant heat input for compensating the heat removal by the electrical wirings and the heat transfer from the mixing vessel to the adiabatic jacket, was usually followed further for $30-60$ min. During these operations, the calorimeter was handled approximately in the same manner as during the mixing process to eliminate the effect of friction of the liquids in the vessel and the torsion of inlet calorimeter cables. It was established that in the range of $0-3\%$ of the total heat of mixing, the error in measuring the "course" of calorimeter did not change.

The drift was loosened after reaching the steady state of the "course" of calorimeter. To prevent a considerable initial undercooling of the mixing vessel at larger heats of mixing (200—500 J) and the consequent immeasurable heat transfer from the adiabatic jacket, it sufficed to choose such a spring that the drift might be captured by the membrane. From several experiments during which both parts of the vessel were filled by the same substance (mixture), it was possible to determine from the decrease in the calorimeter run the heat corresponding to the drift motion and to breaking through the separating foil as $(-0.20) - (-0.35)$ J according to the spring used and to the density of the liquids. At lower values of the heats of mixing (30—50 J), the power input was decreased from usual 1.1 W to 0.4 W which led to the removal of undesirable large heat pulses and to reaching a smooth course of the whole process. The heat transfer into the vessel reached the value corresponding to the "course" of calorimeter after 10—30 min from the beginning of the mixing process and the experiment was stopped.

Errors in the measurements. As the total error of the measurements depends on the errors of single subsequent operations, it is necessary for an estimate of its value to try to determine firstly the partial deviations. The error during the double weighting of the syringe did not exceed 0.05% at sample weights in the range 7—19 g even if the partial volatility of components during filling was considered. Temperature run was always adjusted to a maximum of 1% of the value of the heat of mixing. The uncertainty in its determination may be esrimated according to the time of mixing as $0.1—0.3$ J. The relative error in the determination of the heating input was given by the quality of a QLK compensator as 0.04%. The error in the time measurement by an universal BM 445 E conter is negligible for a correcr adjustment of the frequency in the oscillation generator. The error corresponding to the change in the composition of the vapour phase may be calculated easily[5] if Raoult's and Dalton's laws are assumed to hold. *E. g.* for a methanol–benzene system at 45°C ($x_1 = 0.6855$) it amounts to 0.3 J mol^{-1}, which is less than 0.1%. The situation is similar at other concentrations. For a benzene–cyclohexane system, where the vapour pressures and heats of evaporation of both components differ only little, the error is still less. After taking into account all these circumstances we are entitled to suppose that the total error in measuring the molar excess enthalpy should not exceed the value of $0.3—0.5\%$ for systems with $h^E = 400$ J mol^{-1} or maximally 1% for systems with the heat of mixing of $\sim$100 J mol^{-1}. Despite this it is possible to asses responsibly the accuracy of experimental data only after examining the consistency of the results and by comparing them with best literature data.

RESULTS AND DISCUSSION

Experimentally determined heats of mixing h^E(J mol^{-1}) in dependence on the mol fraction x_1 of alcohol for the methanol–benzene system at 25 and 45°C are given in Table I together with values calculated from a polynomial expansion[6] of the Redlich-Kister type which has the following from at 25 or 45°C, resp.

$$h^E(\text{J mol}^{-1}) = 10^3 x_1(1 - x_1)\,(9.479 - 40.084 x_1 + 93.328 x_1^2 - \\ - 103.808 x_1^3 + 43.28 x_1^4)\,, \tag{1}$$

$$h^E(\text{J mol}^{-1}) = 10^3 x_1(1 - x_1)\,(12.603 - 53.344 x_1 + 126.064 x_1^2 - \\ - 141.344 x_1^3 + 59.136 x_1^4)\,. \tag{2}$$

Even though the maxima on the mixing curves are reproduced by these equation, the result is not too good. The mean absolute percent deviation is by two to three times greater than the assumed error of the measurements. This only confirms the well-known fact that the Redlich-Kister expansion is not adequate for correlating h^E-curves with the maximum shifted pronouncedly to the concentration limit[7,8]. Due to this fact, only "smoothed" h^E-values read off from the graph of the $h^E/x_1(1 - x_1) = f(x_1)$ dependence were used for the comparison with literature data.

The methanol–benzene system at 25°C was measured by several authors, sometimes with considerably different results. After a detailed analysis of types of the calorimeters and methods of the measurement, the data by Mrazek and Van Ness[7] may be considered as most advantageous ones for a comparison (continual dilution calorimeter with an automatic elimination of the vapour phase, error less than 1%). For comparison, the difference between the values of these authors and our "smoothed"

TABLE I

Experimental and Calculated h^E-Values (J mol^{-1})

x_1	h^E	δ	x_1	h^E	δ
		Methanol(1)–benzene(2) system, 25°C[a]			
0·0878	555·9	4·75	0·3986	690·8	1·17
0·1139	603·8	0·07	0·4771	641·0	0·07
0·1720	683·7	−1·14	0·5554	578·1	0·11
0·1784	685·1	−1·68	0·5770	555·2	−0·14
0·1836	690·6	−1·41	0·6400	487·4	0·69
0·2176	712·0	−0·51	0·6678	456·4	1·64
0·2952	720·9	0·80	0·6743	449·5	2·01
0·3009	720·7	0·92	0·6965	424·4	3·09
0·3274	715·2	1·05	0·7009	424·5	4·49
0·3467	711·1	1·28	0·8685	196·5	2·23
0·3627	705·9	1·31	0·8689	194·7	1·57
		Methanol(1)–benzene(2) system, 45°C[b]			
0·0628	599·0	4·54	0·5004	867·6	−0·09
0·0981	753·0	0·65	0·5672	781·8	−1·47
0·1218	812·4	−1·83	0·6751	626·9	0·64
0·1857	925·9	−1·42	0·6816	616·2	0·81
0·2275	958·4	−0·60	0·6827	612·0	0·45
0·2848	974·1	0·47	0·6855	609·3	0·85
0·3368	970·2	1·06	0·7621	475·9	2·75
0·4057	940·0	0·62	0·8667	277·1	−0·57
0·4169	933·9	0·58			

Table I
(continued)

x_1	h^E	δ	x_1	h^E	δ
		Benzene(1)–cyclohexane(2) system, 50°C[c]			
0·2120	478·0	0·03	0·5465	721·1	−0·06
0·2981	599·2	−0·08	0·5969	703·0	−0·13
0·3878	682·9	−0·03	0·6479	670·3	−0·13
0·4463	714·3	0·10	0·7021	620·3	0·14
0·4831	724·1	0·14	0·7879	502·1	0·27
0·5114	725·0	−0·02	0·8531	378·2	−0·29
		Tetrachloromethane(1)–benzene(2) system, 25°C[d]			
0·3561	107·02	−0·71	0·4907	116·38	0·56
0·3659	110·00	0·99	0·4996	115·51	−0·16
0·3890	111·25	0·02	0·5173	115·81	0·34
0·4156	113·38	0·08	0·5380	114·73	−0·01
0·4478	115·49	0·47	0·5501	113·91	−0·23
0·4503	114·52	−0·45	0·5704	113·58	0·56
0·4583	115·37	0·07	0·5950	110·98	−0·01
0·4730	115·55	−0·04	0·6162	108·87	−0·01
0·4791	114·93	−0·65	0·6358	107·70	1·04
0·4804	115·97	0·24	0·6401	105·94	−0·09
0·4897	115·81	0·07	0·6424	105·03	−0·67

Standard deviation (J mol^{-1}): [a] 2·36, [b] 2·93, [c] 0·26, [d] 0·12. Mean absolute deviation (%) between experimental h^E-values and those calculated from Eq. (4): [a]1·46, [b] 1·14, [c] 0·12, [d] 0·34.

h^E-curve is plotted on Fig. 3 in dependence on the mole fraction of methanol. The result is satisfactory. The mean absolute difference for the whole concentration range oscillates around 0·3%, which might confirm correctness of the estimate of the error in our measurements. Heats of mixing measured by Koukol[9] in an isothermal calorimeter (glass mixing vessel, liquids separated by mercury, similar measuring and control systems of the calorimeter as in our case) are on the contrary systematically lower by as much as 4% and do not correspond to a 0·3% error given by the author. Goates, Snow and James[10] and Grolier[11] also used mixing vessels with a metal foil for separating the liquids, their measurements were, however, nonisothermal ones. Their results are on the contrary higher by as much as 4% at 20−60 mol% methanol and they lie outside of the range of their estimated errors (1% or 2%, resp.). Our earlier data[8] are on the average lower by 1·5%, however, in the region of the expected error of 2−2·5%. Experimental data for the methanol–benzene system at 45°C are

by far less abundant. A comparison on Fig. 4 shows again very good agreement with data by Mrazek and Van Ness[7]. The mean deviation of both sets is higher (0·9%), but it lies in the region of errors of both measurements. Data of Williamson and Scott[12] and Brown and coworkers[13] are on the contrary lower by 4−6% in the region of the maximum.

The experimental heats of mixing in the benzene–cyclohexane system at 50°C are in the second part of Table I together with the corresponding mole fractions of benzene. The form of the correlation equation was

$$h^E(\text{J mol}^{-1}) = x_1(1 - x_1)(2868\cdot78 - 113\cdot75x_1 + 350\cdot12x_1^2),\qquad(3)$$

with the mean absolute deviation of $\bar{\delta} = 0\cdot12\%$, maximum deviation 0·28%, and the standard deviation of $\sigma = 0\cdot26$ J mol^{-1}. For comparison, the difference between heats of mixing h^E as given by different authors and h_C^E-values calculated from Eq. (3)
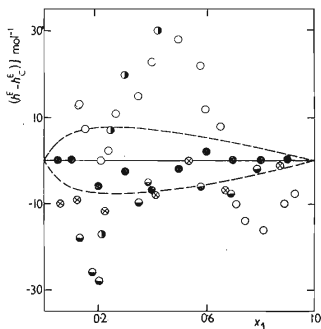

Fig. 3

Comparison of Excess Enthalpies in the Methanol(1)–Benzene(2) System at 25°C

h^E Values of excess enthalpies by different authors, h_C^E values read off from the smoothed curve of our measurements; ● ref.[7], ⊕ ref.[8], ◒ ref.[9], ○ ref.[10], ◐ ref.[11]; dashed curves encompass the region of a 1% deviation.
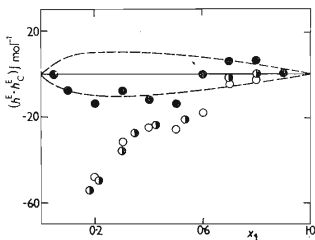
Fig. 4

Comparison of Excess Enthalpies in the Methanol(1)–Benzene(2) System at 45°C, (● ref.[7], ◐ ref.[12], ○ ref.[13])

is again plotted on Fig. 5. The agreement with measurements by Savini and cowor-
kers[14] is excellent $(\delta < 0.4\%)$. The agreement with Lundberg's data[4] is slightly
worse.

The tetrachloromethane–benzene system was proposed by McGlashan[5,15] as
a testing system for calorimeters due to an easy accesibility of both components,
a great difference in their densities and relatively low heats of mixing. The third part
of Table I contains results of our measurements (25°C) in the region of the mole frac-
tion of tetrachloromethane $x_1 = 0.3 - 0.7$ (all h^E values may be measured directly
in this concentration range without using subsequent measurements) together with
deviations δ (%) from the equation

$$h^E(\text{J mol}^{-1}) = x_1(1 - x_1)(509 - 151x_1 + 117x_1^2) \qquad (4)$$

with the standard deviation of 0.12 J mol^{-1} and the mean absolute deviation of
0.34%. The maximum error of 1% corresponds to the estimated error in the measure-
ments.

So that it may be possible to have at least a certain picture of the consistency of the
data, heats of mixing calculated according to Eq. (4) are compared in Table II at seve-
ral values of x_1 with excess enthalpies determined in other laboratories[4,6,14,16-19].
It is obvious from the table that there are essentially two sets of measurements differ-
ing mutually by $1.5 - 2.0\%$. Our data are very close to values given by Larkin and
McGlashan[17], Murakami and Benson[16] and recently by Stokes and coworkers[6].
Even a critical analysis of calorimeters used and the measuring technique does not
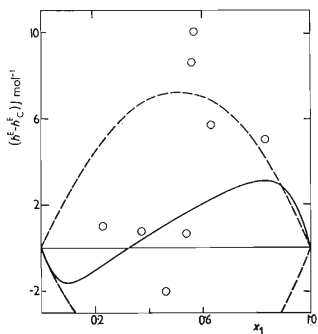suffice to decide unambiguously which of the sets of the data is more reliable. In

FIG. 5

Comparison of Excess Enthalpies in the
Benzene(1)–Cyclohexane(2) System at 50°C,
○ ref.[4], — — ref.[14]

Table II

Calculated Values of the Enthalpy of Mixing h^E(J mol^{-1}) in the Tetrachloromethane(1)–Benzene(2) System at 25°C

The relations were used as given by the corresponding authors.

For x_1	This work Eq. (4)	Ref.[16]	Ref.[17]	Ref.[6]	Ref.[4]	Ref.[18]	Ref.[14]	Ref.[19]
0·30	99·59	100·19	98·91	99·59	98·02	98·21	98·27	97·55
0·34	105·74	106·31	105·60	105·66	104·03	104·23	104·32	103·57
0·38	110·38	110·92	110·26	110·25	108·54	108·81	108·90	108·13
0·40	112·16	112·67	112·05	112·01	110·32	110·57	110·66	109·87
0·44	114·65	115·08	114·55	114·46	112·08	113·06	113·12	112·31
0·48	115·69	116·07	115·63	115·52	113·92	114·18	114·21	113·36
0·50	115·69	116·03	115·65	115·54	113·97	114·23	114·23	113·37
0·54	114·66	114·93	114·63	114·53	113·07	113·32	113·26	112·38
0·58	112·30	112·45	112·21	112·16	110·84	111·05	110·95	110·04
0·60	110·52	110·69	110·47	110·46	109·41	109·41	109·28	108·37
0·64	106·05	106·14	105·94	106·02	104·86	105·09	104·93	104·01
0·68	100·18	100·21	100·01	100·10	99·16	99·38	99·20	98·29
0·70	96·73	96·72	96·50	96·70	95·79	95·99	95·81	94·91
σ	0·12	0·33	0·26	0·06	0·11	0·13	0·18	0·52

agreement with other authors[19,20] we suppose that a substantial influence is here exerted by traces of decomposition products of tetrachloromethane. On using tetrachloromethane of the degree of purity of 99·3%, we measured h^E-values which were systematically lower by 2−3 J mol^{-1}. This only confirms the idea that this system will not be probably in the future, in contrast to original hopes, the most advantageous one for testing mixing calorimeters.

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Translated by K. Hlavatý.