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A flow calorimeter for enthalpies of mixing The enthalpy of mixing of *n*-hexane + cyclohexane at 298.15 K

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A new flow calorimeter for measurements of enthalpies of mixing is described. It has been used to make a series of measurements on *n*-hexane + cyclohexane at 298.15 K with a view to recommending that pair of liquids for checking new calorimeters. The results, including the present ones, obtained as the result of an international cooperative effort in five different laboratories with five quite different calorimeters, reveal no systematic discrepancies and establish the enthalpy of mixing at 298.15 K with a certainty unprecedented in this field. A few measurements have also been made at 313.15 K.

1. Introduction and scope

We have little doubt that thermometrically undisclosed heat leaks are an important source of the discrepancies[1] which, in spite of recent advances,[2–6] are still found among measurements of enthalpies of mixing made in "static" calorimeters. With a flow calorimeter it is possible, by varying the flow rates, to eliminate errors caused by heat leaks. When we began to build a flow calorimeter for enthalpies of mixing the only one which had been described in the literature was that of Rose and Storvick.[7] Since then Sturtevant and Lyons[8] have also described one. We believe that the one described below is a more accurate instrument than either of the previous ones. It is not yet, however, capable of the reproducibility which we [9] and others[2–6, 10, 11] have been able to achieve with static calorimeters. Nevertheless we believe that improvements in design and measurement will eventually lead to flow calorimeters which supersede static calorimeters in this field.

As part of an international effort,[5, 8, 10, 11] arranged by one of us (M.L.M.) for the I.U.P.A.C. Commission on Thermodynamics and Thermochemistry, to find a pair of liquids for which the enthalpy of mixing was sufficiently well established by concordant measurements made in several different calorimeters and in several different laboratories, so that it might be recommended for testing new calorimeters, we have used our flow calorimeter to measure the enthalpy of mixing of the chosen pair of liquids *n*-hexane + cyclohexane at 298.15 K. We have also made a few measurements at 313.15 K so as to obtain a value of the temperature coefficient of the enthalpy of mixing sufficiently accurate for the correction to 298.15 K of measurements made close to but not at that temperature.

2. The calorimeter

A diagram of the calorimeter which was made from Teflon is shown in figure 1. Four inlets lead into a mixing chamber C having a volume of 2.5 cm^3. Liquid A is injected through the two inlets A shown in figure 1, and liquid B through two inlets at right-angles. The terminal 3 mm of each injector tube has a diameter of 1 mm and a cross-section, reduced by the presence of thermocouple leads, of about 0.15 mm^2. With a typical flow rate of 5 mg s^{-1} for each liquid, the liquids enter the mixing chamber with speeds of about 0.015 m s^{-1}, and remain there for about 250 s before flowing out of the calorimeter at D. The disposition and dimensions of the injector

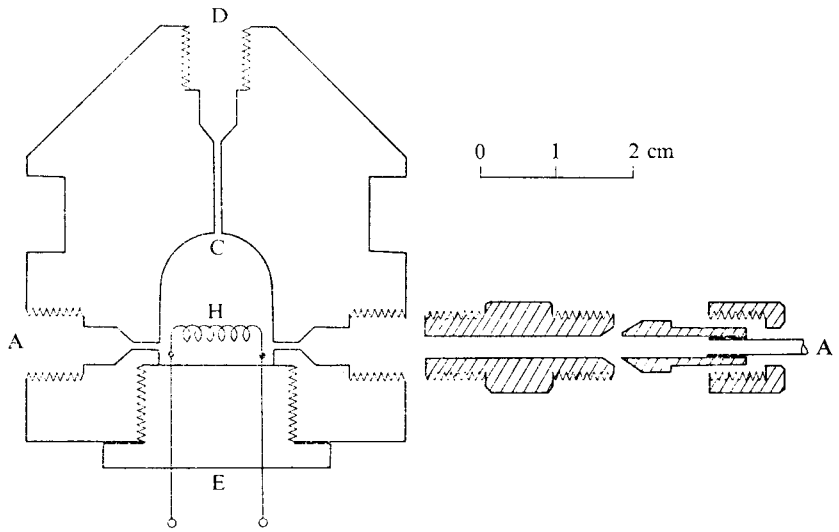

FIGURE 1. The flow calorimeter. Only one of the five brass couplings to the four inlet ports and to the outlet port D of the Teflon calorimeter vessel is shown.

tubes, combined with the size of the mixing chamber and consequent residence time, turned out to be sufficient to ensure complete mixing in the mixing chamber. This was proved by the use of a mechanically driven propeller-stirrer, not shown in figure 1, which was attached to a shaft let through into the mixing chamber from the position E and sealed there by means of a neoprene O-ring. The stirrer was needed only to demonstrate that it was unnecessary, and was not used after the initial testing of the calorimeter.

The resistance coil H (about 3.4 Ω) was used to supply energy to the liquid in the mixing chamber C. Its resistance was measured with a Rosemount VLF 51 a.c. bridge, a correction being made for the resistance of the leads. The current through the coil (from about 30 to 140 mA) was measured with the help of a 10 Ω standard resistor and a potentiometer. Four copper-to-constantan thermocouples were placed each with one junction in the mixing chamber and the other in the cavity near the entrance to the narrow part of one of the injector tubes. They were connected through

high-quality switches to a galvanometer with a photocell amplifier, and could be used to detect temperature differences of about 10^{-4} K. The calorimeter was immersed in an oil-filled thermostat maintained at (298.150 ± 0.003) K.

Liquids A and B were supplied from flowmeters and passed through 2 m of 2 mm i.d. copper tubing immersed in the thermostat before entering the calorimeter. The flowmeters will be described in detail elsewhere. Each consisted of a 900 cm^3 glass flask containing not more than about 400 cm^3 of degassed pure liquid, the rest of the space being filled with vapour. The flask was wrapped with a "permanent" heater (30 to 50 W) and was fitted with an internal "intermittent" heater of bare nichrome wire (22 Ω; 2 to 7 W). The flask was provided with an exit tube through which liquid was driven by its own vapour pressure first through a water-cooled tube, and then in turn through 2 m of 2 mm i.d. copper tubing and 1.5 m of 0.5 mm i.d. glass capillary tubing, both contained in a subsidiary thermostat. A mercury manometer placed across the glass capillary and also contained in the subsidiary thermostat, was used by means of platinum contacts and a relay to control the power supplied to the intermittent heater and so to ensure that the pressure drop across the capillary, and hence the flow rate of liquid through the capillary, were maintained constant. The flowmeters were calibrated by weighing and were found to give flow rates which were almost linear functions of the pressure drop, and which could be reproducibly calculated from the pressure drop to within 0.25 per cent or better for flow rates from about 4 to 9 mg s^{-1}.

In an endothermic mixing experiment the pressure drop across each flowmeter was recorded, and the power P needed just to restore the temperature of the mixed liquids in the mixing chamber C to that of the unmixed liquids was measured. In practice it was found possible to maintain a steady state for 15 min or more. The molar enthalpy of mixing H^E and mole fraction x of liquid B are then given by the formulae

$$H^E = P/(f_A+f_B), \quad x = f_B/(f_A+f_B), \tag{1}$$

where f_A and f_B are the molar flow rates of the liquids A and B.

3. Materials

The results labelled "Series 1" were obtained with British Drug Houses Ltd. "for Spectroscopy" grade liquids. The *n*-hexane was dried over sodium sulphate and fractionally distilled. The cyclohexane was dried over sodium sulphate, refluxed for 3 h over mercury to remove any traces of sulphur compounds, and fractionally distilled. The results labelled "Series 2" were obtained with Phillips Petroleum Ltd. "Research Grade" samples, which were dried over sodium sulphate and distilled before use.

4. Results

The results of the two series of measurements at 298.15 K are shown in table 1. The first column gives the total molar flow rate f, the second the mole fraction x of cyclohexane, and the third the measured value of the molar enthalpy of mixing H^E. The deviation δ given in the last column will be discussed below. The measurements were all made at round values of x since it was easy to adjust each of the flow rates,

TABLE 1. Enthalpy of mixing H^E of mixtures of *n*-hexane + cyclohexane containing mole fraction x of cyclohexane at 298.15 K

$f/10^{-5}$ mol s^{-1}	x	H^E/J mol^{-1}	δ/J mol^{-1}
	Series 1		
6.423	0.250 0	143.8	+0.99
6.880	0.300 0	165.3	+1.54
7.410	0.350 0	181.3	−0.51
8.028	0.400 0	197.4	+0.64
5.078	0.450 0	210.9	+2.48
9.634	0.500 0	216.5	−0.02
5.586	0.500 0	216.9	+0.38
6.207	0.550 0	221.3	+0.52
6.982	0.600 0	221.6	+0.77
7.980	0.650 0	215.8	−0.44
9.311	0.700 0	205.9	−0.62
11.172	0.750 0	190.9	−0.17
		root mean square: 0.96	
	Series 2		
6.880	0.300 0	166.6	+2.84
7.410	0.350 0	182.0	+0.19
8.028	0.400 0	195.8	−0.06
5.586	0.500 0	215.0	−1.52
9.634	0.500 0	217.5	+0.98
6.207	0.550 0	220.0	−0.78
6.982	0.600 0	221.1	+0.27
7.980	0.650 0	216.1	−0.14
		root mean square: 1.14	
		overall root mean square: 1.11	

and hence their ratio, to any desired value. One measurement in Series 2 gave a wildly discordant value and was rejected.

The results of four measurements at 313.15 K are given in table 2 together with the corresponding values at 298.15 K calculated from equation (2) (see below). The temperature coefficient $\partial H^E/\partial T$ is seen to have a value of -1.3 J K^{-1} mol^{-1} at values of x near that at which H^E has its maximum. This low value ensures that it is sufficient to adjust the temperature of the calorimeter only to within about 0.1 K of 298.15 K when using this pair of liquids to check a calorimeter.

TABLE 2. Enthalpy of mixing H^E of mixtures of *n*-hexane + cyclohexane containing mole fraction x of cyclohexane at 313.15 K. The corresponding values of H^E at 298.15 K calculated from equation (2), and values of $\Delta H^E/\Delta T$, are given in the third and fourth columns

x	H^E(313.15 K) / J mol^{-1}	H^E(298.15 K) / J mol^{-1}	$\Delta H^E/\Delta T$ / J K^{-1} mol^{-1}
0.400 0	187	197	−0.7
0.500 0	200	217	−1.1
0.550 0	202	221	−1.3
0.600 0	201	221	−1.3

5. Discussion

Our results, together with those of Watts *et al.*,[5] Sturtevant and Lyons,[8] Marsh and Stokes,[10] and Murakami and Benson,[11] are shown plotted in figure 2 as the

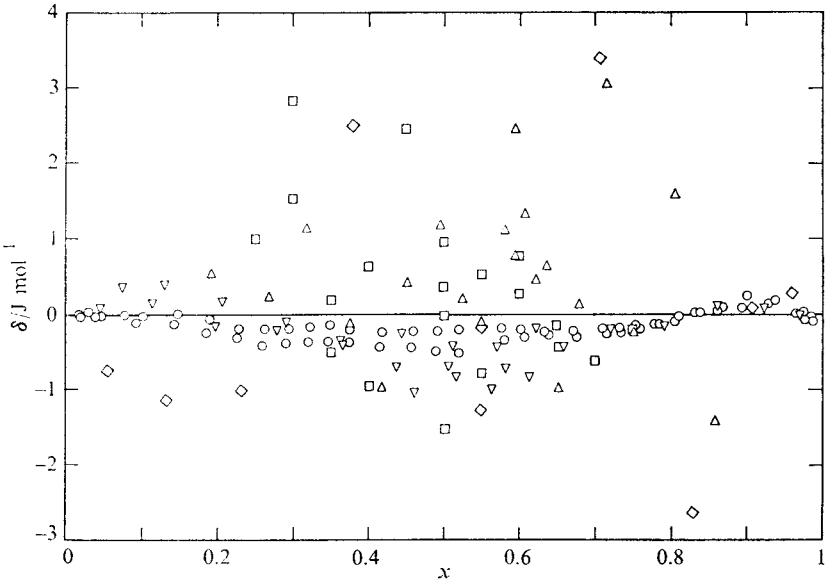

FIGURE 2. The excess δ of the experimental value of the enthalpy of mixing H^E of *n*-hexane+cyclohexane at 298.15 K over that calculated according to equation (2). □, This work; △, Watts *et al.*;[5] ◇, Sturtevant and Lyons;[11] ○, Marsh and Stokes;[10] ▽, Murakami and Benson.[11]

excess δ of the experimental value of H^E over that calculated from the equation

$$H^E/\mathrm{J\,mol^{-1}} = x(1-x)\{866.10-249.4(1-2x)+97.0(1-2x)^2-31.8(1-2x)^3\}, \quad (2)$$

which was fitted to all the results by the method of least squares, all points being equally weighted. The values of δ calculated from our results are given together with their root mean squares in the last column of table 1. The results of our Series 2 are less extensive and slightly less accurate than those of Series 1 because, having forgotten that a U.S. pint is considerably smaller than a U.K. pint, we had insufficient of the pure liquids. The root mean square values of δ for the five independent sets of measurements are given in table 3 together with the overall value.

Although our accuracy is appreciably better than that of Sturtevant and Lyons, and at least as good as that of Watts *et al.*, it is clear from figure 2 and table 3 that we have been outclassed by Murakami and Benson and by Marsh and Stokes. Murakami and Benson have achieved an accuracy comparable with that which we were able to achieve[9] with our own static calorimeter. Marsh and Stokes, in a prodigious series of measurements, have achieved a reproducibility appreciably better than has ever been achieved before in measurements of enthalpies of mixing.

TABLE 3. Root mean square deviations of several series of measurements of H^E for *n*-hexane + cyclohexane at 298.15 K from equation (2)

Authors	No. of points	$\langle\Sigma\delta^2\rangle^{1/2}$/J mol^{-1}
Watts *et al.*[5]	21	1.18
Sturtevant and Lyons[8]	10	1.71
Marsh and Stokes[10]	63	0.23
Murakami and Benson[11]	27	0.48
This work (Series 1)	12	0.96
This work (Series 2)	8	1.14
This work (Series 1 + 2)	20	1.11
Overall	141	0.81

More importantly, however, it is clear from figure 2 that the results obtained in five different laboratories with five quite different calorimeters show no systematic discrepancies. The pair of liquids *n*-hexane + cyclohexane with H^E given at 298.15 K by equation (2) can therefore be recommended for checking new calorimeters with a confidence considerably greater than that which any such recommendation could previously have been made.

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