

APPLICATION OF A FLOW MICROCALORIMETER TO DETERMINE THE EXCESS ENTHALPIES OF BINARY MIXTURES OF NON-ELECTROLYTES*

REIJI TANAKA**, PATRICK J. D'ARCY AND GEORGE C. BENSON

Division of Chemistry, National Research Council of Canada, Ottawa K1A 0R6 (Canada)

(Received 23 September 1974)

ABSTRACT

The performance of an LKB flow microcalorimeter has been improved through changes in the auxiliary equipment and operating technique. Measurements of excess enthalpies, precise to 0.5% or better, are reported for several test systems.

INTRODUCTION

In recent years there has been an increasing interest in the use of flow calorimetry to study the enthalpies of mixing of non-electrolytes¹⁻⁸. With flow techniques it is possible to avoid several of the difficulties which may arise in batch and dilution calorimeters of more conventional design. In particular, it is unnecessary to use mercury to separate the component liquids before mixing, and the mixing can readily take place in the absence of any vapor space. In addition, any desired composition is obtained directly by setting the relative flow-rates of the components, and transient effects during the initial formation of the mixture are unimportant.

Several research groups³⁻⁷ have used the LKB flow microcalorimeter (Model 10700-1) to determine enthalpies of mixing of non-electrolytes. Tests of the performance of this calorimeter, by comparison of measurements on several systems with results from the literature, indicate a lower precision (particularly at the ends of the mole fraction range) than has been achieved with the best batch or successive dilution calorimeters.

The present paper describes an attempt to improve the precision of the LKB flow microcalorimeter through changes in the auxiliary equipment and operational technique. The performance of the calorimeter was examined by measuring enthalpies of mixing for the systems benzene + cyclohexane, cyclohexane + n-hexane, benzene + carbon tetrachloride and *p*-dioxane + carbon tetrachloride at 298.15 K.

*Issued as NRCC No. 14412.

**National Research Council of Canada Postdoctorate Fellow, 1973-1975.

EXPERIMENTAL

Equipment

The prototype of the LKB flow microcalorimeter has been described by Monk and Wadsö⁹ and the main features of the commercial instrument have been reviewed recently by Harsted and Thomsen⁶. Preliminary work with our instrument, as supplied by the manufacturer, indicated the desirability of making a number of changes in the equipment. These are outlined in the following paragraphs.

Thermostatic air-bath. The temperature control of the air-bath containing the calorimetric unit was improved by installing a larger cooling coil consisting of 8 m of 0.8 cm ID copper tubing and by using a Thermotrol controller (Hallikainen Instruments, Model 1053A) to operate the heater. The best location for the sensor coil of the Thermotrol was found to be in the air stream exiting from the main chamber of the air-bath. The temperature of the bath was monitored with a quartz thermometer (Hewlett-Packard, Model 2801 A) positioned near the sensor. During operation of the calorimeter at 298.15 K the room temperature was maintained at 298.15 ± 0.3 K and water at 294.15 ± 0.05 K was circulated through the cooling coil. The temperature of the air-bath could be controlled to ± 0.005 K and the temperature of the calorimeter heat sink remained constant within ± 0.035 K over periods of several weeks. With a steady flow of liquid, the maximum change of the thermopile baseline voltage was less than $0.3 \mu\text{V}$ in 1 h.

Thermopile circuit. The response of the calorimeter thermopile was digitized by feeding the signal after amplification by a Keithley 150B amplifier, to a recorder (Texas Instruments, Servo/riter II) and a digital voltmeter (Digital Measurements, Model DM 2001) in parallel. The output from the latter was connected to a printer (Anadex, Model DP-650), and registered every 10 sec.

Calibration circuit. The calorimeter heater circuit was modified to provide a digital measure of the current. This was accomplished by installing a digital voltmeter (Velonex, Impac Series 45) to monitor the potential difference across a calibrated resistor in series with the heater. Using three different resistors (selected by a switch) the current could be measured with an error of less than 0.03% over the whole range of interest.

Pumps and flow system. The peristaltic pumps recommended by the manufacturer of the flow microcalorimeter were unsuitable for handling the variety of organic solvents encountered in our work. Several commercial syringe pumps were tried but none of these gave pulseless flows steady enough for the present application; furthermore it was difficult to preset them to produce a mixture with any specified composition.

More satisfactory liquid flows were obtained with a pair of piston displacement pumps designed and constructed in the shops of the NRCC. The flow from each of these units is produced by the linear displacement of an accurately ground stainless steel piston (1.59 cm OD) which is pushed through a tight Teflon seal into a water-jacketed glass cylinder (1.90 cm ID) containing the liquid. The piston is moved by a

precision screw (approximately 15.7 threads per cm) which is rotated by a variable speed DC motor (Bodine Electric, Type NSH-12) coupled to it through a gear box with four manually selectable ratios. A transparent disk with 120 equally spaced radial photomasked sectors is mounted on the shaft of the motor and a light beam passing through the disk falls on a slit with a phototransistor mounted behind it. The sine wave output from the phototransistor is fed to a Schmidt trigger and the resulting pulses drive counting and averaging circuits which provide digital readouts of the total number of counts and of the number of counts per second. A signal from the averager is also fed back through an operational amplifier and power transistors to control the speed of the motor. Over most of the working range (150 to 1500 r.p.m.) speeds are controlled to about 0.1%.

For each pump, the flow-rate, Q , is related to the gear ratio, G , and the reading, S , of the averager circuit (i.e., the motor speed in counts per second) by the equation

$$Q = K_p GS \quad (1)$$

where K_p is a constant characteristic of the pump. With the present gear train and size of piston, K_p is approximately equal to $4 \times 10^{-5} \text{ cm}^3 \text{ count}^{-1}$ and the maximum flow-rate is about $0.12 \text{ cm}^3 \text{ sec}^{-1}$. The gear box provides reduction of the flow by factors of 0.1, 0.01 and 0.001. Two different methods were used to determine the value of K_p . In one, the pump was operated at a known speed and the time to fill a calibrated volume was determined. In the other, the liquid delivered for a known number of counts was collected and weighed. Calibrations done by the two methods, using both water and di-butyl phthalate, agreed within 0.1%.

Previous workers^{4,6} have reported difficulties due to bubbles collecting in the flow system. Originally we experienced similar troubles. We found that the liquids must be degassed before use and that all tubing must be clean and free from dust and grease. Sharp irregular edges at joints between metal and plastic tubing appeared to act as nuclei or traps for bubbles. Less bubbles occurred after the thin wall Teflon tubing supplied with the calorimeter was replaced by heavy wall tubing of a slightly larger size (No. 17 American wire gauge).

Changes in back pressure in the flow system caused variations of the thermopile voltage. These were eliminated by allowing the liquid to overflow at the outlet from a vertical tube mounted about 10 cm below the level of the calorimetric unit.

Technique

Principle of measurement. The LKB flow microcalorimeter uses a twin design to minimize the effects of fluctuations in the temperature of the heat sink. However, the two cells differ internally, and the twin principle cannot be used satisfactorily to cancel frictional effects associated with the flow. Monk and Wadsö⁹ pointed out that the thermopile baseline varies with the flow-rate and viscosity of the calorimetric liquid. In our work, liquid flowed only through the "mixing cell"; the other cell was empty and its inlet and outlet were connected.

The basic equation for a steady state, in which a power, W , is released within the calorimetric cell by electrical heating or a mixing process, is

$$W = \varepsilon[\mathcal{V}_L(f) - \mathcal{V}_L^0(f)] \quad (2)$$

The notation $\mathcal{V}_L(f)$ is used to indicate the thermopile voltage when there is a volume flow-rate, f , of the calorimetric liquid, L; $\mathcal{V}_L^0(f)$ is the baseline voltage associated with the flow alone. The value of the thermopile calibration constant, ε , can be obtained from the change in thermopile voltage corresponding to the dissipation of a known electrical power in the heater. For a constant volume flow of the same calorimetric liquid, ε is constant within 0.1% for heating currents from 2 to 30 mA. However, ε varies with the flow-rate and the volumetric heat capacity C_L of the calorimetric liquid according to the relation

$$\varepsilon \equiv \varepsilon(f, C_L) = \varepsilon^0 [1 + \alpha f C_L] \quad (3)$$

where ε^0 is the thermopile constant for zero flow and α is a constant characterizing the exchange of energy between the cell and the heat sink. The quantities 1 and $\alpha f C_L$ are, respectively, proportional to the fractions of the power W dissipated to the heat sink and carried out of the cell by the liquid flow. For normal operating conditions, Monk and Wadsø⁹ found that $\alpha f C_L$ was less than 0.03.

Experimental results for the calibration constant determined at several flow-rates for liquids with different volumetric heat capacities are given in Fig. 1. The

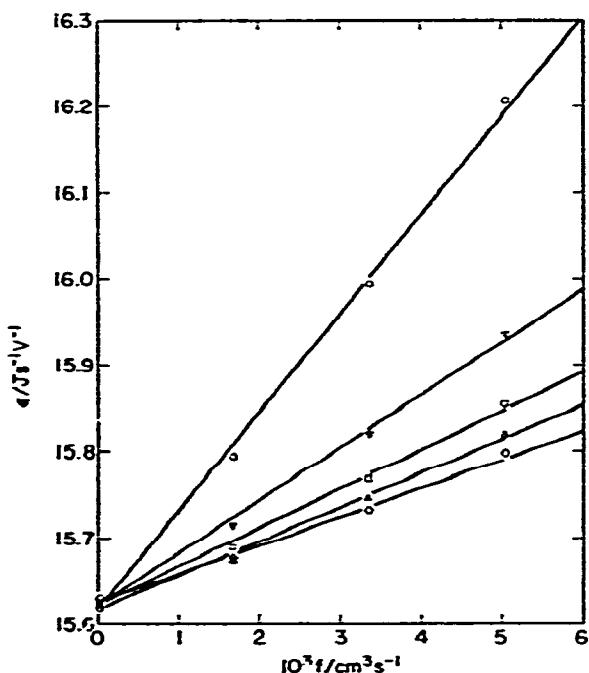


Fig. 1. Variation of thermopile calibration constant, ε , with volume flow-rate, f , for various liquids. ○, Water; ▽, tert.-butyl alcohol; □, p-dioxane; △, tetrahydrofuran; ◇, carbon tetrachloride.

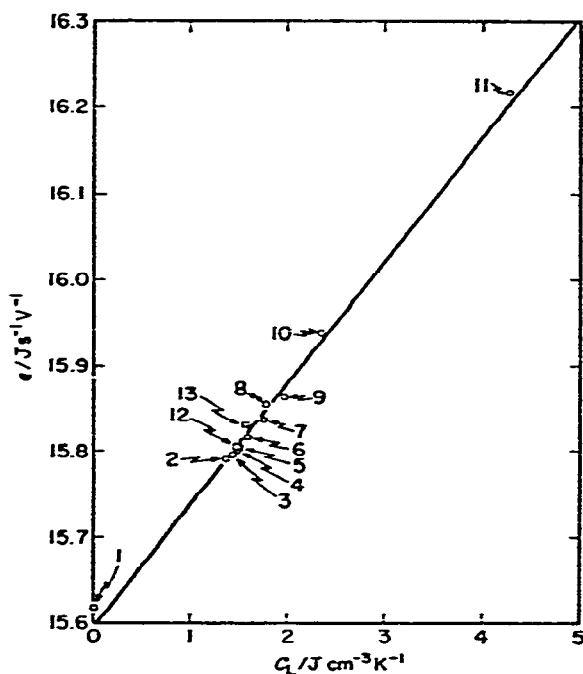


Fig. 2. Variation of thermopile calibration constant, ε , with volumetric heat capacity, C_L , at constant volume flow-rate, $f = 5 \times 10^{-3} \text{ cm}^3 \text{ sec}^{-1}$ of liquid. 1 = Air (i.e., no liquid); 2 = carbon tetrachloride; 3 = cyclohexane; 4 = n-hexane; 5 = benzene; 6 = tetrahydrofuran; 7 = methyl ethyl ketone; 8 = *p*-dioxane; 9 = cyclohexanol; 10 = tert.-butyl alcohol; 11 = water; 12 = benzene + cyclohexane mixture, $\phi_1 = 0.5$; 13 = *p*-dioxane + carbon tetrachloride mixture, $\phi_1 = 0.5$.

relation between the calibration constant and volumetric heat capacity at a constant flow-rate of $0.005 \text{ cm}^3 \text{ sec}^{-1}$ is illustrated in Fig. 2. Within the experimental error of about 0.1%, ε varies linearly with both f and C_L , and the values of ε^0 obtained from the intercepts in the two plots agree reasonably well.

In a binary mixture formed by combining volume flows, f_1 and f_2 , of the components, the volume fraction of component i is

$$\phi_i = f_i / (f_1 + f_2) \quad (4)$$

based on the unmixed state, and the corresponding mole fraction is

$$x_i = (f_i / V_i) / [(f_1 / V_1) + (f_2 / V_2)] \quad (5)$$

where V_i is the molar volume of component i . We have found it convenient to work at a constant total flow for the unmixed components ($f_1 + f_2 = 0.005 \text{ cm}^3 \text{ sec}^{-1}$). The flow-rates of mixtures with different mole fractions then differ due to the volume of mixing, but these variations are usually less than a few per cent. Determinations of the calibration constant $\varepsilon(f, C_M)$ and the baseline voltage $\mathcal{V}_M^0(f)$ for each mixture, M , greatly prolong the time taken for a run and require relatively large amounts of the component liquids. Fortunately, in many cases it is possible to approximate these

values for the mixture from the results of measurements on the pure components at a volume flow-rate of $f_1 + f_2$.

If the volume of mixing is small,

$$f \simeq f_1 + f_2 \quad (5)$$

and if the excess heat capacity is also small

$$C_M \simeq \phi_1 C_1 + \phi_2 C_2 \quad (7)$$

where C_i is the volumetric heat capacity of pure i . Under these circumstances, it follows from eqn (3) that

$$\varepsilon(f, C_M) \simeq \phi_1 \varepsilon(f_1 + f_2, C_1) + \phi_2 \varepsilon(f_1 + f_2, C_2) \quad (8)$$

Two values of $\varepsilon(f, C_M)$ measured for equivolume mixtures are plotted in Fig. 2 at values of C_M calculated from eqn (7); the agreement with the data for pure liquids supports the utility of eqn (8) for systems with excess heat capacities less than $10 \text{ J mol}^{-1} \text{ K}^{-1}$.

The base line voltage due to the liquid flow alone can be attributed to two effects. There is a power associated with the flow of liquid into the cell since the temperature of the liquid entering the cell from the heat exchanger mounted in the heat sink differs slightly from the final steady state temperature of the cell. This input power is proportional to the volume flow and the volumetric heat capacity of the liquid, as in the case of the power loss through the liquid flowing out of the cell, but will differ from the latter if the temperature imbalance differs. Assuming eqns (6) and (7) to be valid, the baseline voltage due to this effect for a mixture will be the volumetric average of the baselines for the pure liquids at the same flow-rate

$$\mathcal{V}_M^0(f) \simeq \phi_1 \mathcal{V}_1^0(f_1 + f_2) + \phi_2 \mathcal{V}_2^0(f_1 + f_2) \quad (9)$$

The other effect contributing to the baseline voltage is the release of thermal energy due to the action of frictional forces in the cell. It has been reported⁶ that the power developed by frictional forces at a fixed flow-rate is directly proportional to the viscosity. Assuming that the viscosity of a mixture can be approximated by the volume average of the viscosities of its components would again suggest the use of eqn (9) to approximate the frictional contribution to $\mathcal{V}_M^0(f)$. However, our work indicates that this contribution is more complex and that, in addition to viscosity and flow-rate, it depends on other factors. Thus frictional effects appear fairly abruptly at a particular flow-rate for the liquid and then increase significantly with the flow-rate. For viscous liquids at flows greater than the critical values, estimate of the frictional contribution for a mixture from the contributions for the components is subject to a relatively large uncertainty. For the systems studied in the present investigation the baseline voltages were all small at the flow-rate used, and estimation of $\mathcal{V}_M^0(f)$ by means of eqn (9) leads to an uncertainty in H^E of 0.1 J mol^{-1} at most.

Operational procedure. Samples of the component liquids, partially degassed by agitation under reduced pressure, were loaded into the pumps and forced through the tubing and mixing cell. There appears to be a lack of symmetry in the construction of our cell, since it was found that steadier mixing lines were recorded when the denser liquid was introduced via one particular inlet tube. All measurements were made with the sum of the flow-rates of the components equal to $5.000 \times 10^{-3} \text{ cm}^3 \text{ sec}^{-1}$, and it was possible to set the motor speed and gear ratio to produce any mole fraction within an estimated error of 0.0005.

First the baseline was measured for one component. To avoid thermal effects due to diffusive mixing, some of the component to be used was forced back from the mixing cell into the tubing from the other pump, which was disconnected briefly. After a steady baseline was registered on the printer for about 10 min, a steady electrical heating was applied and the thermopile calibration constant was determined. Next, thermopile equilibrium voltages were established for a number of mixtures, and finally the baseline and calibration constant were measured for the other pure component.

The values of the molar excess enthalpies of the mixtures were calculated from the relation

$$H^E = \varepsilon(f, C_M) [\mathcal{V}_M(f) - \mathcal{V}_M^0(f)] / [(f_1/V_1) + (f_2/V_2)] \quad (10)$$

using the approximate eqns (8) and (9) for $\varepsilon(f, C_M)$ and $\mathcal{V}_M^0(f)$. Uncertainties in the values of H^E arising from systematic errors in the thermopile voltages and flow-rates were estimated to be less than 0.2%.

TEST MEASUREMENTS

The systems benzene (1) + cyclohexane (2), cyclohexane (1) + n-hexane (2), benzene (1) + carbon tetrachloride (2), and *p*-dioxane (1) + carbon tetrachloride (2) were used to investigate the suitability of the calorimeter for measurements of the enthalpies of mixing of non-electrolytes. Descriptions of the component liquids are given in Table 1, where values of their densities and refractive indices are listed, along with data from the literature¹⁰ for comparison.

The results of the determinations of H^E at 298.15 K are summarized in Table 2. Each set was fitted with the smoothing equation

$$H^E (\text{J mol}^{-1}) = x_1 (1 - x_1) \sum_{p=1}^n a_p (1 - 2x_1)^{p-1} \quad (11)$$

by the method of least squares, assigning equal statistical weights to all points. Choice of the appropriate number n of coefficients a_p was based on the variation of the standard error of the estimate defined by

$$\sigma = [\sum \{H_{\text{obs.}}^E - H_{\text{calc.}}^E\}^2 / \{n_{\text{obs.}} - n\}]^{1/2} \quad (12)$$

where the sum was taken over the $n_{\text{obs.}}$ results for the set. The coefficients and standard

TABLE 1

DENSITIES ρ AND REFRACTIVE INDICES n_D OF COMPONENT LIQUIDS AT 298.15 K

Component	Source	Purification	ρ ($g\ cm^{-3}$)		n_D	
			Obs.	Lit. ¹⁰	Obs.	Lit. ¹⁰
Benzene	Fisher Scientific Co. Cert. ACS spectra- nalyzed reagent	gas chromatography	0.87363	0.87370	1.49783	1.49792
Cyclohexane	Fisher Scientific Co. Cert. ACS spectra- nalyzed reagent	gas chromatography	0.77374	0.77389	1.42350	1.42354
n-Hexane	Phillips Petroleum Co. Pure grade reagent	gas chromatography	0.65480	0.65481	1.37222	1.37226
Carbon tetra- chloride	Baker Chemical Co. GC-spectro- photometric quality	used without further treatment	1.58432	1.58439	1.45722	1.45739
<i>p</i> -Dioxane	Fisher Scientific Co. Cert. ACS reagent	vacuum sublimation	1.02775	1.02797	1.41971	1.42025

TABLE 2

EXPERIMENTAL RESULTS FOR MOLAR EXCESS ENTHALPIES H^E AT 298.15 K

x_1	H^E ($J\ mol^{-1}$)	x_1	H^E ($J\ mol^{-1}$)	x_1	H^E ($J\ mol^{-1}$)
C_6H_6 (1) + C_6H_{12} (2)		$C_4H_8O_2$ (1) + CCl_4 (2)		C_6H_6 (1) + CCl_4 (2) ^a	
0.0500	148.52	0.0500	-35.76	0.0500	22.30 ^a
0.1000	281.47	0.1000	-73.06	0.0500	22.40
0.1500	399.11	0.1500	-107.62	0.1000	42.37 ^a
0.2000	501.52	0.2000	-140.98	0.1000	42.36
0.2500	590.25	0.2500	-170.75	0.1500	59.71 ^a
0.3000	661.86	0.3000	-196.31	0.1500	59.50
0.3500	719.75	0.3500	-217.43	0.2000	74.62 ^a
0.4000	762.28	0.4000	-233.73	0.2000	74.48
0.4500	789.07	0.4500	-243.99	0.2500	87.03 ^a
0.5000	800.65	0.5000	-246.05	0.2500	87.01
0.5500	796.68	0.5000	-245.73	0.3000	97.14 ^a
0.6000	777.68	0.5500	-245.52	0.3000	97.09
0.6500	741.98	0.6000	-238.44	0.3500	105.06 ^a
0.7000	691.52	0.6000	-238.24	0.3500	105.13
0.7500	622.62	0.6500	-226.01	0.4000	111.04 ^a
0.8000	536.86	0.7000	-207.88	0.4000	110.80
0.8500	432.51	0.7000	-207.77	0.4500	114.28 ^a
0.9000	308.72	0.7500	-184.40	0.4500	114.28
0.9500	165.06	0.8000	-155.55	0.5000	116.08 ^a
		0.8000	-155.33	0.5000	115.96 ^a

(Continued on page 171)

TABLE 2 (continued)

x_1	H^E (J mol ⁻¹)	x_1	H^E (J mol ⁻¹)	x_1	H^E (J mol ⁻¹)
<i>C₆H₁₂</i> (1) + <i>C₆H₁₄</i> (2)					
0.0500	33.34	0.8500	-122.29	0.5000	116.02
0.1000	64.16	0.9000	-84.85	0.5500	115.28 ^a
0.1500	92.57	0.9000	-84.77	0.5500	115.22 ^a
0.2000	118.64	0.9500	-43.65	0.5500	115.28
0.2500	142.46			0.6000	112.60 ^a
0.3000	163.40			0.6000	112.32 ^a
0.3500	181.39			0.6000	112.38
0.4000	196.54			0.6500	107.35 ^a
0.4500	207.16			0.6500	107.14
0.5000	215.58			0.7000	99.64 ^a
0.5500	219.73			0.7000	99.65
0.6000	219.82			0.7500	89.73 ^a
0.6000	220.30			0.7500	89.85
0.6500	216.06			0.8000	77.44 ^a
0.7000	206.42			0.8000	77.43
0.7500	191.36			0.8500	62.55 ^a
0.8000	169.53			0.8500	62.55
0.8500	140.22			0.9000	44.82 ^a
0.9000	103.21			0.9000	44.85
0.9500	56.64			0.9500	24.01 ^a
				0.9500	24.11

^a Two separate runs were carried out. Results from the first run are marked with superscript a; those from the second are unmarked.

TABLE 3

VALUES OF COEFFICIENTS FOR eqn (11) DETERMINED BY THE METHOD OF LEAST SQUARES

System	a_1	a_2	a_3	a_4	a_5	σ (J mol ⁻¹)
<i>C₆H₆</i> (1) + <i>C₆H₁₂</i> (2)	3202.75	-164.10	119.99	-43.71		0.37
<i>C₆H₁₂</i> (1) + <i>C₆H₁₄</i> (2)	862.91	-251.12	105.26	-32.43		0.29
<i>C₆H₆</i> (1) + <i>CCl₄</i> (2)	463.81	-14.64	31.11	-3.65		0.11
<i>C₄H₈O₂</i> (1) + <i>CCl₄</i> (2)	-987.77	58.59	151.69	43.85	42.74	0.58

error for each representation are listed in Table 3. Deviations of the experimental results from their smoothed representations are plotted and compared with other data from the literature in Figs. 3-6.

Benzene (1) + *cyclohexane* (2). It can be seen from Fig. 3 that our results for this system agree with those determined by successive dilution calorimeters^{11,12} within $\pm 0.5\%$ over all of the mole fraction range.

Cyclohexane (1) + *n-hexane* (2). This system has been recommended by the IUPAC Commission on Thermodynamics and Thermochemistry¹³ as a standard for testing calorimeters for heats of mixing. In Fig. 4, our results are in excellent agree-

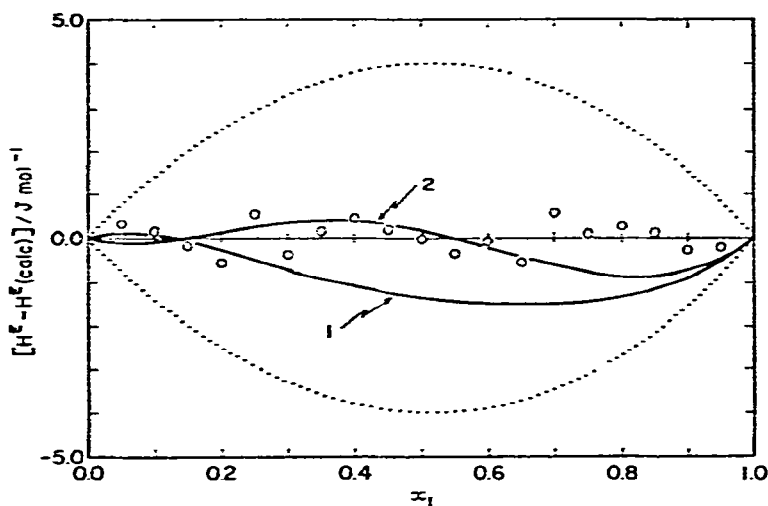


Fig. 3. Difference plot for excess enthalpies of benzene (1) + cyclohexane (2) at 298.15 K. \circ , Experimental results. Curves: 1, Stokes et al.¹¹; 2, Murakami and Benson¹². Dotted curves represent $\pm 0.5\%$ deviation.

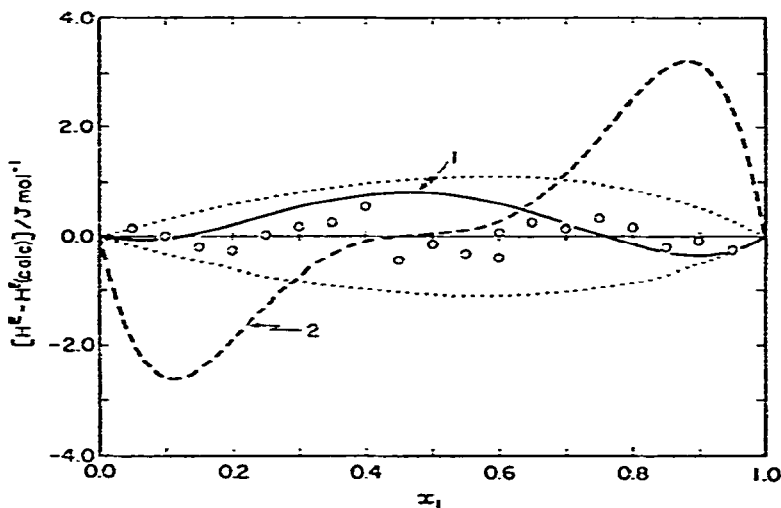


Fig. 4. Difference plot for excess enthalpies of cyclohexane (1) + n-hexane (2) at 298.15 K. \circ , Experimental results. Curves: 1, McGlashan and Stoekli²; 2, Grolier et al.⁸. Dotted curves represent $\pm 0.5\%$ deviation.

ment with the smoothing function proposed by McGlashan and Stoekli² to represent the results of five independent investigations.

Harsted and Thomsen⁶ have also reported measurements with an LKB flow microcalorimeter on this system over a very restricted mole fraction range ($x_1 = 0.44$ to 0.51). Their results have not been plotted in Fig. 4 since they have a wide scatter exceeding 10 J mol^{-1} .

Curve 2 in Fig. 4 represents the deviations of results obtained recently in our laboratory with a Picker dynamic flow microcalorimeter⁸ which scans an entire H^E curve in about 20 min. Although the results from this other commercial calorimeter agree well with the present measurements around $x_1 = 0.5$, discrepancies amounting to several per cent occur towards the ends of the mole fraction range, and it appears that accuracy has been sacrificed for speed of operation.

Benzene (1)+carbon tetrachloride (2). The large difference between the densities of the components of this system provides a good test of the efficiency of the mixing in a calorimeter. In Fig. 5, our results agree with those of other workers^{11,12,14} (see curves 1-3) to within $\pm 0.5\%$ over most of the mole fraction range. Somewhat

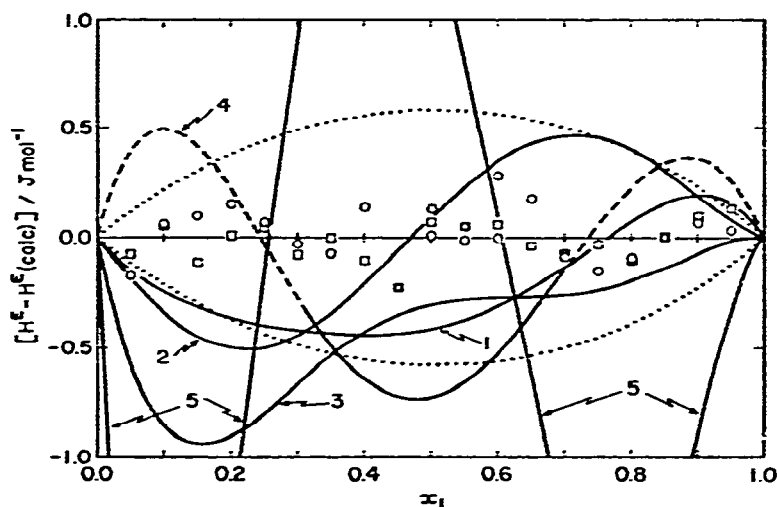


Fig. 5. Difference plot for excess enthalpies of benzene (1)+carbon tetrachloride (2) at 298.15 K. Experimental results: O, Run 1; □, run 2. Curves: 1, Stokes et al.¹¹; 2, Murakami and Benson¹²; 3, Larkin and McGlashan¹⁴; 4, Joly and Philippe³; 5, Gustin and Renon^{4,15}. H^E (J mol^{-1}) = $x_1(1-x_1)[469.7 + 6.62(1-2x_1) - 10.7(1-2x_1)^2 - 58.0(1-2x_1)^3]$. Dotted curves represent $\pm 0.5\%$ deviation.

larger discrepancies occur at mole fractions below $x_1 = 0.2$, but since our results are higher than the literature values, it seems likely that these discrepancies should be attributed to differences in the purity of the components and not to poor mixing. This conclusion is supported by the good agreement between the results from the two separate runs.

Curve 4 in Fig. 5 represents the results obtained by Joly and Philippe³ who also used an LKB flow microcalorimeter, and measured six mixtures in the range $x_1 = 0.27$ to 0.69. Their results are more scattered than ours and the standard error of the estimate reported for their smoothing function is four times larger.

Other measurements on benzene+carbon tetrachloride using an LKB calorimeter have been carried out by Gustin and Renon⁴. They presented their results only

graphically* and reported a root mean square deviation of 1 J mol^{-1} . However, it can be seen from their plot that in some cases the deviations of individual measurements from their smoothing equation are as high as 2 J mol^{-1} and that some of the deviations from our results are larger still.

p-Dioxane (1) + carbon tetrachloride (2). There is no exothermic system which has been investigated thoroughly enough to be recommended as a standard. *p*-Dioxane + carbon tetrachloride was selected because it had been studied previously in our laboratory^{1,2}. In Fig. 6, our new results are roughly 1.5 to 3% higher than those obtained previously. We believe that much of this discrepancy can be attributed to

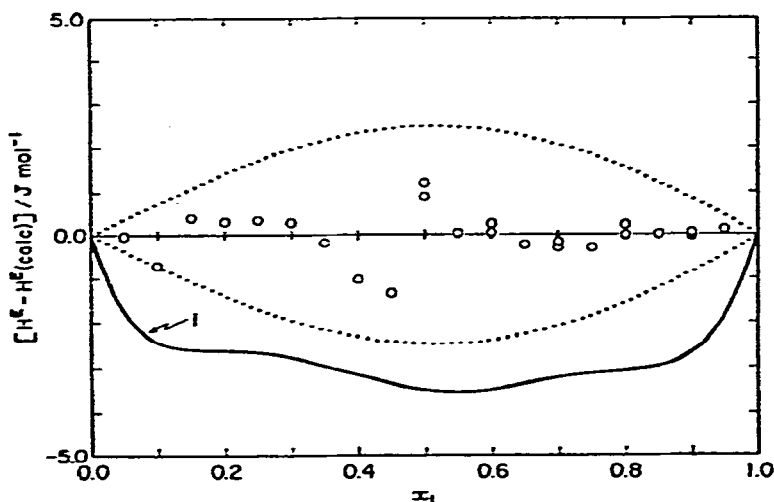


Fig. 6. Difference plot for excess enthalpies of *p*-dioxane (1) + carbon tetrachloride (2) at 298.15 K. O, Experimental results. Curve: 1, Murakami and Benson^{1,2}. Dotted curves represent $\pm 1.0\%$ deviation.

differences in the component liquids used for the two investigations. In particular, *p*-dioxane is difficult to purify and to store. Our calorimetric measurements were carried out within 10 h of the preparation of the sample of *p*-dioxane, and measurements repeated at several mole fractions were in excellent agreement.

CONCLUSION

The changes in the equipment and operating technique described in this paper have led to a substantial improvement in the precision and accuracy of measurements of H^E with the LKB flow microcalorimeter over that reported by other workers³⁻⁶.

*Correspondence with Professor Renon^{1,5} indicates that Fig. 1 in ref. 4 is incorrect due to a misinterpretation of the smoothing function of Larkin and McGlashan (in eqn (2) of ref. 14, x was taken to be the mole fraction of benzene instead of the mole fraction of carbon tetrachloride). This error vitiates the comparison with the results of Larkin and McGlashan but the relative positions of the other sets of data are still significant.

For systems similar to the test systems, with $|H^E(0.5)| \geq 100 \text{ J mol}^{-1}$, the precision is estimated to be better than 0.5%, and in fact compares favorably with the precision of the best batch and successive dilution calorimeters. The close agreement of our results with those measured in other types of calorimeters suggests that our measurements for the first three test systems are accurate to about 0.5%. It therefore appears that the LKB calorimeter can be used to advantage for precise studies on a wide variety of binary non-electrolyte systems. However, measurements of small H^E values for systems with components which vary widely in viscosity will not be as precise, due to uncertainties in the determination of the baseline voltage.

ACKNOWLEDGEMENTS

We are indebted to a number of the staff of the NRCC for their assistance in the design and construction of the piston displacement pumps used in this research. In particular, we wish to acknowledge the contributions of M. Hamel (Plant Engineering Central Drafting Service), L.L.T. Bradley (Division of Physics Electronics Group), and A. Couture (Division of Chemistry Instrument Laboratory). We also wish to thank O. Kiyohara, J.-P. E. Grolier, and M. R. Peterson for carrying out preliminary studies with the LKB calorimeter.

REFERENCES

- 1 J. M. Sturtevant and P. A. Lyons, *J. Chem. Thermodyn.*, 1 (1969) 201.
- 2 M. L. McGlashan and H. F. Stoeckli, *J. Chem. Thermodyn.*, 1 (1969) 589.
- 3 R. D. Joly and R. Philippe, *J. Chim. Phys. Physicochim. Biol.*, 69 (1972) 783.
- 4 J.-L. Gustin and H. Renon, *J. Chem. Eng. Data*, 18 (1973) 164.
- 5 S. Murakami, R. Tanaka and R. Fujishiro, *J. Solution Chem.*, 3 (1974) 71.
- 6 B. S. Harsted and E. S. Thomsen, *J. Chem. Thermodyn.*, 6 (1974) 549.
- 7 B. S. Harsted and E. S. Thomsen, *J. Chem. Thermodyn.*, 6 (1974) 557.
- 8 J.-P. E. Grolier, G. C. Benson and P. Picker, *J. Chem. Thermodyn.*, 7 (1975) 89.
- 9 P. Monk and I. Wadsö, *Acta. Chem. Scand.*, 22 (1968) 1842.
- 10 J. A. Riddick and W. B. Bunger, in A. Weissberger (Ed.), *Organic Solvents*, Vol. II of *Techniques of Chemistry* Wiley-Interscience, New York, 1970.
- 11 R. H. Stokes, K. N. Marsh and R. P. Tomlins, *J. Chem. Thermodyn.*, 1 (1969) 211.
- 12 S. Murakami and G. C. Benson, *J. Chem. Thermodyn.*, 1 (1969) 559.
- 13 IUPAC Commission on Thermodynamics and Thermochemistry, *Bull. Thermodyn. Thermochem.*, 13 (1970) 507.
- 14 J. A. Larkin and M. L. McGlashan, *J. Chem. Soc.*, (1961) 3425.
- 15 H. Renon, private communication.