Microflow Calorimeter Design for Heats of Mixing

Microflow calorimeter design for heats of mixing is surveyed. Precise temperature equilibration of the fluids before mixing, the elimination of frictional energy effects from the instrument response, and the absence of flow-rate and physical-property-dependent heat leaks are particularly important. A design using a differential mode of operation is based on a careful analysis of entropy generation in flows with mixing and friction. The compensation for frictional heating and the lack of dependence of measurements on flow rate and mixture physical properties other than h^E represents a major advance. Measured data for the well-tested cyclohexane-hexane system had an average deviation of only 0.41%. For the more viscous cyclohexane-1-hexanol system, measured data of similar precision are considered the best available.

J. D. Raal and P. A. Webley
Department of Chemical Engineering
University of Natal
Durban 4001, South Africa

Introduction

The design of an accurate microflow calorimeter capable of handling systems with large physical property variations is a very challenging proposition since the data and procedures are subject to numerous potentially serious errors. No systematic analysis of equipment design and performance is available. The purpose of this publication is to examine several important aspects of microflow calorimeter design for measuring heats of mixing and to show how incorporation of the proposed features produces an instrument capable of providing accurate and precise data for both viscous and nonviscous systems.

The commercial development of microflow pumps capable of delivering small, nearly pulse-free flows with excellent accuracy and reproducibility (for liquid chromatography), and the ease with which these can produce liquid mixtures in any proportion in the absence of a vapor space and without any special accommodation for volume changes on mixing has lately favored the development of flow-type calorimeters for measurement of excess enthalpy.

The majority of the data in the literature have been measured on batch-type calorimeters. The best types are capable of excellent accuracy, and among the best known are those of Larkin and McGlashan (1961), Mrazek and Van Ness (1961), Winterhalter and Van Ness (1966), Christensen et al. (1968, 1973), and their subsequent variants. Batch-type instruments do not lend themselves readily to automation and, unless carefully designed and operated, are subject to several possible sources of error. The presence of even a small vapor space (common in earlier types) will lead to considerable error, particularly with volatile liquids. Adiabatic types necessarily require a heat leak equal to the stirrer energy input, and because of the slightly raised temperature a small correction, for which the added component heat capacity must be known, is required (Savini et al., 1966). The stirrer energy can be balanced by allowing this small temperature rise of the calorimeter contents above ambient, or in isothermal types can be compensated with a built-in thermoelectric cooler. The stirrer energy input need then not be taken into account provided the second component is added in an amount such that the density and viscosity of the mixture and therefore the stirrer energy input at constant speed are not altered appreciably in any single addition step. In extreme cases, such as that of dimethyl acetamide-water shown in Figure 1, the mixture viscosity is nearly doubled for a mole fraction change of 0.05 in the water-rich region. Accurate accounting for the stirring energy, which is proportional to density at high Reynolds number and to viscosity at low Reynolds number, then becomes problematical even for very small additions of the mixing component.

For the McGlashan-type calorimeter it is not certain that the energy dissipated by inverting the vessel is exactly reproducible. Data obtained by Savini et al. (1966) on the system benzene-carbon tetrachloride differ systematically from those of Larkin and McGlashan (1961).

Remarkably little attention has been given to several impor-

Correspondence concerning this paper should be addressed to J. D. Raal.
The present address of P. A. Webley is Chemical Engineering Dept., MIT, Cambridge, MA 02139.

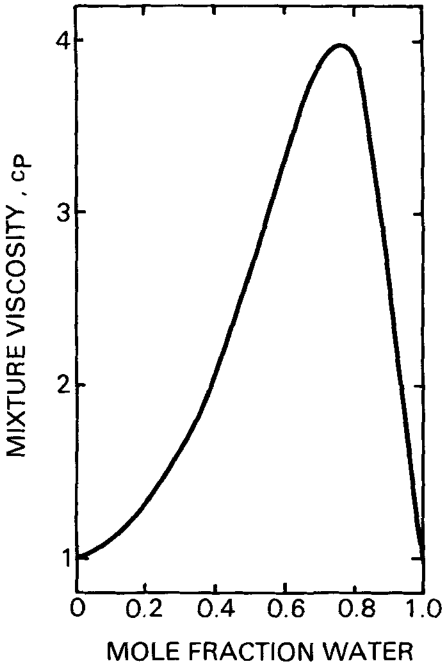

Figure 1. Viscosity of N,N-dimethylacetamide–water solutions at 24°C.
Data of Peterson (1960)

tant requirements for sound design of an accurate microflow calorimeter, and design precepts lack a rigorous base from which improved performance may be sought. The authors believe that a flow calorimeter capable of accuracy rivaling, and perhaps surpassing, that of the best batch instruments can now be designed. Examination of the open literature suggests that no flow calorimeter developed so far meets the basic requirements for a versatile instrument that can handle a variety of systems with widely differing physical properties.

The important basic requirements, in addition to the absence of a vapor space and careful composition control, are considered to be:

1. Carefully designed equilibrators preceding the mixing section and producing both components at exactly the set calorimeter temperature at all flow rates and independent of fluid heat transfer properties.
2. A mixing section that will reduce the intensity of segregation (or some other appropriate measure of mixedness) at all points over the exiting flow cross section to a negligible value for all flow rates used for systems with wide ranges of density, viscosity, and molecular diffusivity; stagnant fluid entrapments should be avoided.
3. Accurate separation of frictional energy from the desired excess enthalpy.
4. Correct accounting for the effect of pressure on excess enthalpy where appropriate.
5. The elimination of heat leaks dependent on fluid flow rates and physical properties.

An additional very useful requirement not previously proposed is that the instrument should also produce mixture heat capacities to permit at least limited thermodynamic consistency testing of the measured excess enthalpies. These aspects are examined in detail below and lead to the design described in detail.

Temperature Equilibration of Fluids Before Mixing

The majority of existing flow calorimeters employ passive heat exchange sections preceding the mixing section in which, typically, the fluids to be mixed are passed through coiled tubes in a constant-temperature bath, (Elliot and Wormwald, 1976; Picker et al., 1969; McGlashan and Stoeckli, 1969; Siddiqi and Lucas, 1982) or are passed through heat exchange tubing soldered to the calorimeter or to the exit tubing (Sturtevant and Lyons, 1969; Goodwin and Newsham, 1971; Christensen et al. 1976, 1981; Gill and Chen, 1972). The approach of the pumped fluid temperature to that of the constant-temperature bath or set calorimeter temperature is a straightforward heat transfer problem, but one that surprisingly has not been examined for microflow calorimeters. The substantial error that can accrue with failure to equilibrate one or both fluids to the calorimeter temperature before mixing ($=\Sigma Cp\Delta T$) is evident, and a convincing demonstration of the sensitivity of the calibration constant to fluid flow rate, and the improvement produced when substituting active for passive heat exchangers, has recently been given by Randzio and Tomaszkiewicz (1980). With active heat exchangers under automatic temperature control the pure fluid temperatures become substantially independent of the flow rate and heat exchange properties of the fluid, but equipment cost is escalated considerably.

The approach of the fluid temperature to that of the bath in which a coil is submerged is conveniently calculated via the heat exchanger effectiveness, ϵ. For a constant temperature heat source the ratio of thermal capacities $C_{min}/C_{max} = 0$ and $\epsilon = 1 - e^{-UA/C_{min}}$ for any flow configuration. For an initially cold fluid ($T = T_{c,in}$) absorbing heat from the bath ($T = T_h$) the temperature defect is then

$$\Delta T(=T_h - T_{c,out}) = e^{-U_oA_o/C_{min}}(T_h - T_{c,in}) \tag{1}$$

To illustrate the errors to be expected, overall heat transfer coefficients were determined for typical flow rates ranging from 0.5 to 5.0 cm^3/min in 1.59 mm OD stainless steel tubing (ID = 1.31 mm) for coils of 0.5, 1.0, and 2.0 m length with a nominal coil radius of 10 cm. Values of U_o and the temperature defect obtained from Eq. 1, together with the calorimeter error are shown in Table 1 for a sample of fluids with widely different physical properties. In the calculation of U_o the heat transfer rate from the coil surface to the bath fluid (water) was estimated using the equation of Chilton et al. (1944):

$$\frac{h_cD_j}{k} = 0.87\left(\frac{L^2N\rho}{\mu}\right)^{2/3}\left(\frac{C_p\mu}{k}\right)^{1/3}\left(\frac{\mu}{\mu_w}\right)^{0.14} \tag{2}$$

Using typical values for paddle length (L = 4 cm) and stirring rate (N = 300 rpm) gives h_c = 1,260, a value assumed to be constant in subsequent calculations. Elimination of the heat transfer resistance between coil and bath fluid (h_c = 0), e.g., when tubes are soldered to a constant-temperature heat sink, will reduce the temperature defects to about half the values shown in Table 1.

Heat transfer from the pumped fluid to the coil wall is invariably by laminar convection, and the Sieder-Tate equation, corrected for the tubing curvature according to McAdams (1942),

Table 1. Temperature Defect and Calorimeter Error in Flow through 1.59 mm OD SS Tubing in Water Bath

Material	Viscosity $\mu^{20°C}$ Pa · s × 10^3	Prandtl No. $Pr^{20°C}$	Flow Rate cm^3/min	Coil Length m	Temp. Defect ΔT K	Error = $MC_p\Delta T/1{,}000$ J/gmol
Benzene	0.627	7.14	5.0	2	0.00025	0.03
			0.5	1	~0	~0
			2.0	1	0.00004	~0.01
			5.0	1	0.0150	1.96
Freon 12	1.45	15.7	5.0	2	0.00188	0.22
			2.0	1	0.00045	0.05
			5.0	1	0.0499	5.88
			2.0	0.5	0.0205	2.42
			5.0	0.5	0.3833	45.19
Isopropanol	2.31	39.8	5.0	2	0.00197	0.32
			0.5	1	~0	~0
			2.0	1	0.00046	0.08
			5.0	1	0.0546	3.61
			2.0	0.5	0.0221	69.39
			5.0	0.5	0.4245	
Cyclohexanol	72	738	5.0	2	0.0003	0.04
			2.0	1	~0	~0
			5.0	1	0.0156	2.71
			5.0	0.5	0.3994	69.71

Initial temperature difference, 10°C

was used:

$$h_i = h_{ST}\left(1 + 3.5\frac{D_i}{D_H}\right) \tag{3}$$

where h_{ST} is the value from the Sieder-Tate equation, and D_i, D_H are the tube and helix diameters, respectively.

The temperature defects in Table 1 are seen to be substantial for the higher flow rate (5.0 cm^3/min) for all substances when using a heat transfer coil of 1 m length or less. The results in Table 1 are numerically independent of the direction of heat transfer if the viscosity correction factor in the heat transfer equations is neglected, as is done in the present study. For rapid estimation of the temperature defect for other organic liquids, data are well correlated (±5%) by a plot of ln $(\Delta T/\Delta T_o)$ vs. $(\alpha L/\dot{V})^{2/3}$ as shown in Figure 2. This equation form is derivable from Eq. 1 assuming the coil inside heat transfer coefficient to form the controlling resistance. Separate linear plots are given for high-density, low-heat-capacity chlorinated hydrocarbons and other nonchlorinated organics.

For endothermic systems failure of the fluid, if initially cold, to reach the set calorimeter temperature will give high values for the excess enthalpy, whereas an initially warm fluid will produce low values; i.e., measurement errors will be compounded in a series of experiments over a temperature range in which the fluids are both heated and cooled before mixing. The variable error that can be introduced, due to say a tenfold flow rate variation required to cover the complete mole fraction composition range, is evident from the very rapid rise in temperature defect with flow rate and may be relatively more serious in the dilute range where h^E is small and the compound flow rates are near their limits.

Thoroughness of Mixing

Unless the mixing process is continued until the mixed fluid composition is uniform on at least a submicroscopic scale, the correct enthalpy of mixing cannot be obtained in any instrument. In a batch calorimeter the mixing process must be continued for a time sufficiently long to reduce the intensity of segregation I_s to an effectively zero value at all points in the calorimeter, not merely in the vicinity of the temperature sensing elements. It is likely, although debatable (Nauman and Buffham, 1983), that slow molecular diffusion is necessary to achieve homogeneity on a molecular or near-molecular scale in a stirred fluid. Brodkey (1967) indicates for example that for high Schmidt number systems (large viscosity and/or small molecular diffusivity) the decay time of concentration intensity increases rapidly with decrease in Reynolds number. Stagnant pockets or boundary layers not subject to eddies (e.g., in a batch calorimeter) could be expected to participate in the homogenizing process by a diffusional mechanism exponential in time with a rate constant such that the detector signal may dwindle to a value detectable only by very precise instrumentation. Failure to account fully for a very small signal over a comparatively long time span could then introduce appreciable error. A proper calibration procedure using a precisely known electrical energy input should eliminate or reduce such errors. It should be recalled, however, that the Lewis number, reflecting relative rates of heat and mass transfer, is generally far from unity for liquid systems, and the diffusion-limited production and dissipation of mixing energy may be subject to a different time constant from that of an electrical calibration procedure.

In a flow calorimeter for any fluid pair the mixed fluid must reach complete homogeneity ($I_s = 0$) before reaching the downstream temperature sensor, at all flow rates required to span the full composition range. For reasons similar to those given above, stagnant pockets should be eliminated from the flow path.

For the majority of the microflow calorimeters in the literature having, typically, an internal tube diameter of 1.31 mm or less in the mixing section, turbulence cannot be sustained except at flow rates well beyond the capacity of most commercial microflow pumps. For laminar systems the reduction of striation

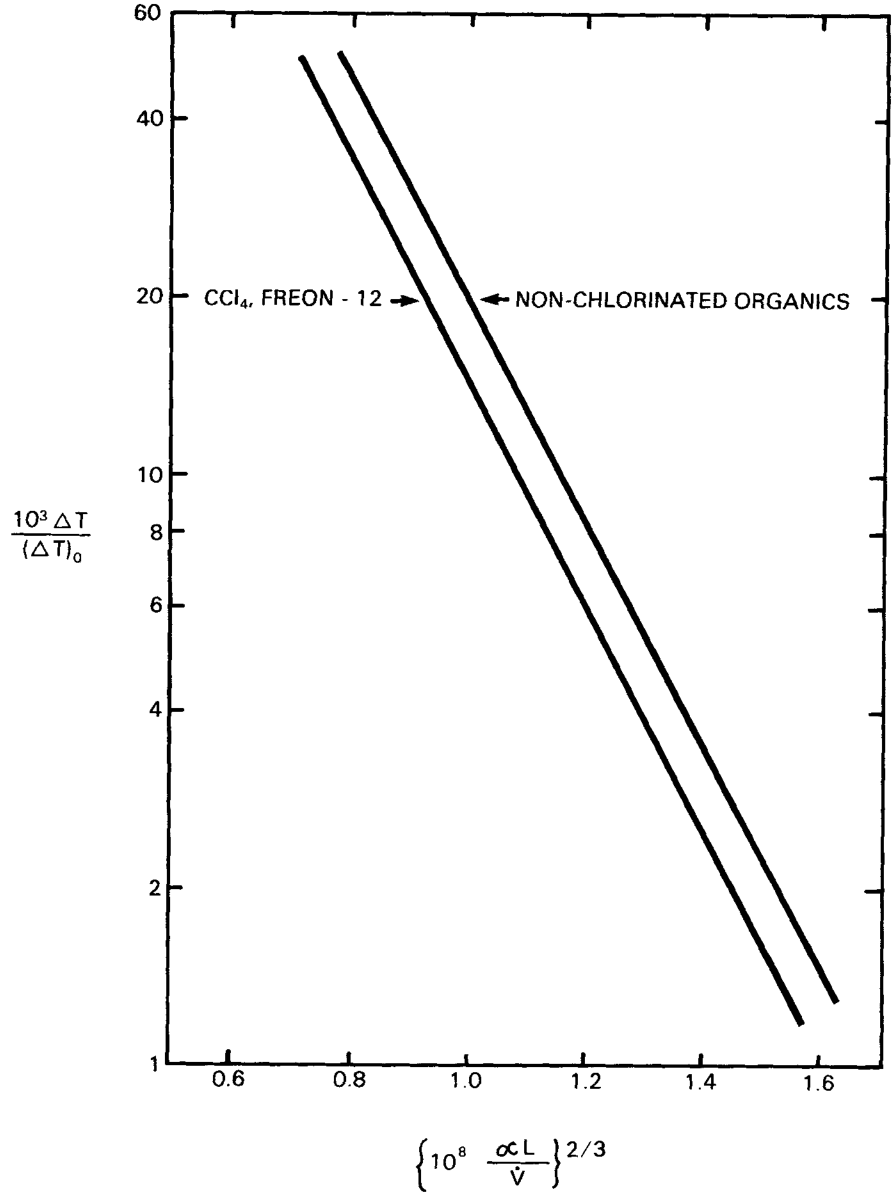

Figure 2. Dimensionless temperature defect as a function of ($\alpha L/\dot{V}$).
α, L in SI units, $\dot{V}$ in mL/min

thickness and intensity of segregation is most effectively accomplished by motionless mixers of the alternating helix type (Naumann and Buffham, 1983; Chen and McDonald, 1973), which produce continuing flow division and radial flow inversion. Such designs are difficult to engineer on a microscale, and the fluid dynamics of their operation is so complicated that detailed numerical analysis of their performance via the equations of motion, although possible in principle is not worthwhile in practice. (The difficulty in analysis derives partly from destruction of tangential symmetry, which elevates the problem to one in three-dimensional space.)

The design of the mixing sections of flow calorimeters has received comparatively little attention, as is evident from the range of devices used by various workers. It is doubtful whether the mixing chambers of McGlashan and Stoeckli (1969) and Randzio and Tomaszkiewicz (1980) or the very short mixing tubes (10 and 15 cm, respectively) of Rose and Storvick (1966) and of Picker et al. (1969) will produce adequate mixing for other than easily mixed systems. The considerable lengths of small-diameter (1.59 mm OD) stainless steel tubing (2 and 1.52 m, respectively) packed with crimped stainless steel wire used by Siddiqi and Lucas (1982) and Christensen et al. (1976, 1981) are more likely to produce good mixing if tightly packed. For systems of appreciable viscosity these long mixing paths are likely to produce considerable pressure drop, and the frictional energy generation, ignored by these authors, may produce substantial error unless carefully corrected or designed for.

It should be noted that an apparent invariance of calibration constant or measured excess enthalpy with flow rate level noted by some authors does not necessarily imply proper functioning of the calorimeter. In endothermic systems, for example, improved mixing (apparent increase in h^E) from a progressive increase of total flow rate will be balanced by an apparent decrease in h^E from an initially hot fluid increasingly failing to reach the set calorimeter temperature through an inadequate passive equilibrator.

Separation of Frictional and Mixing Energy

Microflow calorimeters employ static mixers in which the energy required to mix the fluids is taken directly from the pressure energy of the flowing fluid mixture. Viscous or difficult-to-mix systems may require substantial energy to produce microscale homogeneity, and the attendant large pressure drop may represent dissipation energy significant relative to the excess enthalpy to be measured. For typical organic liquids or mixtures the frictional energy dissipation ranges from about 7–11 J/gmol · atm or, in terms of temperature rise, about 0.05 to 0.08°C per atmosphere pressure drop. This may amount to considerably more than 10% of the enthalpy of mixing for some systems, particularly in the dilute concentration regions. This error source alone may account for the many discrepancies in published heat of mixing data and is considered by the authors to be the principal unsolved problem in flow calorimetry. Somewhat extreme examples of data discrepancy are shown for two difficult-to-mix systems in Figures 3a and 3b.

A further consequence of large frictional pressure drop is the influence of pressure level on the measured excess enthalpy. This influence is generally small and is discussed further below.

Microflow calorimeters typically have reference sections through which the already mixed fluid is passed and which are supposed to be similar to the mixing section, in which a sufficient quantity of measured electrical energy is added to compensate for the excess enthalpy in endothermic systems. The criterion for similarity is usually unstated and often unclear. The present authors believe that the proper use of a reference section is to eliminate frictional effects from the principal instrument response, which should be sensitive only to the enthalpy of mixing and independent of fluid flow rates and physical properties. Remarkably, no known instrument at present satisfactorily eliminates or compensates for frictional heating. The closest approach to proper compensation to eliminate frictional heating from the equipment response is that of Elliot and Wormald (1976). These authors employed mercury manometers and attempted to compensate for unequal pressure drops in the supposedly identical calorimeter sections by calculation. The manometers limited the permissible flow to 0.32 m mol/s for the relatively inviscid benzene-cyclohexane system studied. A relatively crude procedure based on addition of screens was subsequently incorporated by Wormald (1977) in a gas microflow calorimeter. The correction by Elliot and Wormald (1976) for the change of enthalpy with pressure is, however, incorrect and inconsistent with their assumption of zero excess volume.

A much more satisfactory procedure, incorporated in the design described below, is to ensure equality of energy dissipation by accurate pressure drop adjustment in the reference section according to the expressions given below.

To accurately separate frictional and mixing energy in flows with simultaneous mixing and frictional pressure drop it is necessary to relate frictional dissipation to observed pressure drop, fluid flow rates, and physical properties. The preferred approach is to proceed from the macroscopic energy and entropy balances. This approach has been presented in detail elsewhere (Raal, 1986), and only some results and conclusions will be summarized here.

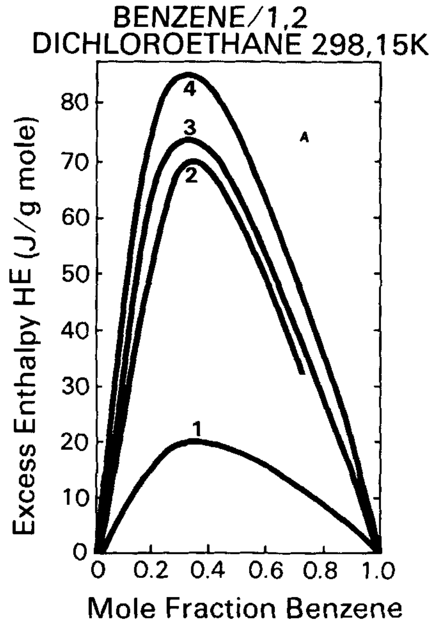

Figure 3a. **Examples of data discrepancy.**

1. Kireev et al. (1937)
2. Tamres (1952)
3. Ruiter (1955)
4. Kireev (1937)

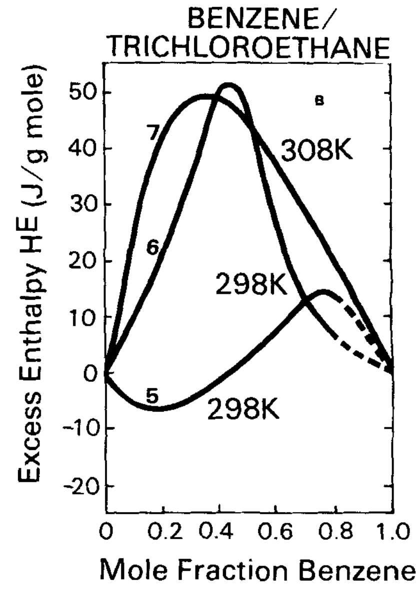

Figure 3b. **Examples of data discrepancy.**

5. Abello (1983)
6. Turner et al. (1970)
7. Patel et al. (1979)

In the static mixer in Figure 4, pure fluids A and B enter at equal temperatures and pressures but at different flow rates $\dot{m}$. Completely mixed fluid AB, after being returned to the initial temperature T_1, passes through the reference section where the observed pressure drop $(p_3 - p_4)$ due to friction causes a small temperature rise to T_2. The macroscopic energy and entropy

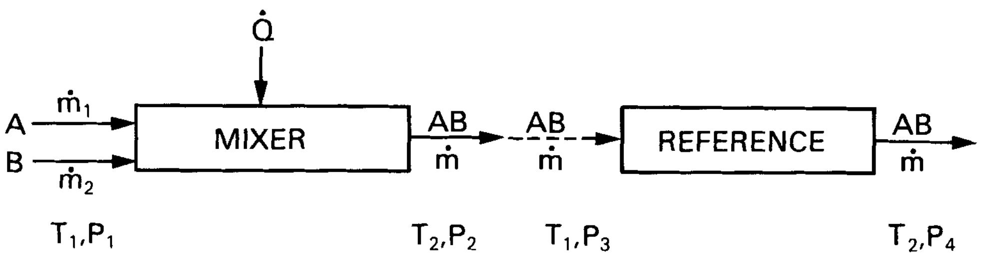

Figure 4. Mixing and reference sections

balances for an open system apply:

$$\sum_{in} \dot{m}(h + u_b^2/2 + gZ) - \sum_{out} \dot{m}(h + u_b^2/2gZ) + \dot{Q} = 0 \quad (4)$$

$$\dot{S}_{gen} + \sum_{out} \dot{m}s - \sum \dot{m}s - \dot{Q}/T \quad (5)$$

The frictional "lost work," ℓw_f is obtained by subtracting from the total entropy generation $T\dot{S}_{gen}/\dot{m}$, the amount due to heat transfer and that due to the mixing process, readily shown to be equal to g^E.

The sequence of mixing and pressure drop in a flow calorimeter is unknown and unpredictable, and a general resolution of Eqs. 4 and 5 for the mixing section is impossible. Solutions can, however, be obtained for the two limiting cases in which:

1. Isobaric isothermal mixing at temperature T_1 is complete before frictional effects are manifested (easy-to-mix systems), and
2. The pure fluids A, B experience a frictional pressure drop *and temperature* rise before mixing, with the mixing now at the slightly higher temperature T_2. The frictional enthalpy and entropy changes in this case are those for the pure (unmixed) fluids. This behavior would be approached with difficult-to-mix systems, for example, where density and viscosity differences between the two components are large.

The results for the frictional energy loss for the two cases obtained by detailed evaluation of enthalpy and entropy changes along appropriate paths are (Raal, 1986):

Case A, easy-to-mix

$$\ell w_f = V_1(p_1 - p_2) \quad (6)$$

where V_1 is the specific volume at temperature T_1. This result is readily confirmed by much simpler procedures once complete isobaric isothermal mixing is assumed as the initial step in the mixer module.

Case B, difficult-to-mix

$$\ell w_f = (p_1 - p_2)(V_2 - V^E) \quad (7)$$

It is of considerable interest to note that the pressure drop now contains the multiplier $(V - V^E)_{T-T_2}$ involving the excess volume V^E.

In practice, mixing and viscous flow dissipation should lie between the extremes of initially complete mixing and the reverse sequence, i.e., between cases A and B. Since in general $V \gg V^E$ the differences are small and a general definition of the lost work can be written as

$$\ell w_f = (p_1 - p_2)(V - FV^E) \quad (8)$$

The ease-of-mixing factor F, with a value between zero and unity, is a complex function of calorimeter geometry, flow rate, and system physical properties and cannot be predicted. It can, in principle, be measured in experiments with pure and fully mixed fluids at the same total flow rate and by using a suitable model for pressure drop (or effective viscosity), in two-phase liquid flows. The results of such studies in our program will be communicated in a later publication.

It may be noted that for difficult-to-mix systems ($F = 1$) the pressure drops in the mixing and reference sections of a flow calorimeter, even if geometrically identical, will not in general be equal and indeed should differ considerably for systems such as that shown in Figure 1. This implication has not previously been recognized.

The results in Eqs. 6 and 7 were obtained by neglecting potential and kinetic energy differences across the mixer (which can in any case be made negligible by experimental design) and by assuming that $C_p \neq f(T)$, $\alpha[=(1/V)(\partial V/\partial T)_p] \neq f(p)$ over the pressure and temperature ranges involved. In the development of the equations for case B it has also been assumed that temperature and pressure are uniform over a cross section at the end of the frictional flow path in the mixer module, an assumption involving somewhat more approximation for the temperature than the pressure.

It is evident from the above results that equal viscous dissipation in the mixing and reference arms of a calorimeter can be effected by equal pressure drop adjustment, for case A, or by adjustment according to Eq. 7 for difficult-to-mix systems.

Since electrical input to the mixing section—the principal measurement—is usually regulated via temperature measurements from thermocouples or thermistors, the small temperature rise due to viscous dissipation in the mixing and reference arms of a calorimeter must be examined for accurate work. In many flow calorimeters (Rose and Storvick, 1966; Sturtevant and Lyons, 1969; Siddiqi and Lucas, 1982) frictional effects were simply neglected and energy input was regulated to maintain isothermal operation.

The temperature rises in the mixing and reference arms of a flow calorimeter are readily obtained from Eq. 4 for cases A and B. For exactly equal pressure drops in the two modules and with electrical energy input equal to the excess enthalpy ($\dot{m}h^E = \dot{Q}$) in the first module, for example, the respective temperature rises (denoted by subscripts I and II, respectively) are:

$$\text{Case A} \quad (T_2 - T_1)_I = (T_2 - T_1)_{II} \quad (9)$$

$$\text{Case B} \quad \frac{(T_2 - T_1)_I}{(T_2 - T_1)_{II}} = \frac{V}{V - V^E} \cdot \frac{C_p - C_p^E}{C_p} \quad (10)$$

The correction term in Eq. 10 can again be generalized in terms of the ease-of-mixing factor F:

$$\frac{(\Delta T)_I}{(\Delta T)_{II}} = \frac{V}{V - FV^E} \cdot \frac{C_p - FC_p^E}{C_p} \quad (0 \leq F \leq 1) \quad (11)$$

Equations 8 and 11 present a soundly based starting point for developing strategies for the separation of frictional and mixing energy in flow calorimeters. For systems and conditions approximating case A (easily mixed systems, $F \sim 0$) for example, it is only necessary to ensure, by adjustment, equal pressure drops in the mixing and reference arms. Thermistor or thermocouple signals from the two modules can then be subtracted in a suitable null device to give a null output signal, independent of viscous flow dissipation, for regulating the electrical input to the mixer.

For systems and conditions approximating case B (difficult-to-mix, $F \sim 1$), development of a proper strategy for eliminating frictional effects is considerably more complicated and requires knowledge of V^E, F, and C_p^E at all compositions to be studied. As an approximation, V^E may be neglected and, for equal pressure drops, temperature rises in the mixing and reference modules can be adjusted to satisfy the ratio $(\Delta T)_I/(\Delta T)_{II} \doteq 1 - F(C_p^E/C_p)$ by electronic means. Alternatively, data measured with equal temperature and pressure drops in the two modules could be corrected with a computer software package based on Eq. 11.

It seems desirable to develop a flow calorimeter design that will produce both h^E and mixture heat capacity (from which C_p^E is directly obtainable) at every mixture composition, since $C_p^E(T)$ data are useful for at least limited thermodynamic consistency testing of the measured data.

Influence of pressure on excess enthalpy

From the pressure dependence of the excess enthalpy

$$\left(\frac{\partial h^E}{\partial P}\right)_T = V^E - T\left(\frac{\partial V^E}{\partial T}\right)_p = V^E(1 - \alpha^E T)$$

the correction for h^E, measured at the average calorimeter pressure $\bar{p}$, to its value at atmospheric pressure P_a is given by:

$$\begin{aligned} h_{P_a}^E &= h_{\bar p}^E - \int_{P_a}^{\bar p} V^E(1 - \alpha T)\,dp \\ &\doteq h_{\bar p}^E - V^E(1 - \alpha^E T)(\bar p - p_a) \end{aligned} \quad (12)$$

The correction is generally small and can safely be neglected except for measurements at high pressures.

Elimination of heat leaks

The authors have found, for isothermal operation, surprisingly, that heat leaks principally through the heating element lead-

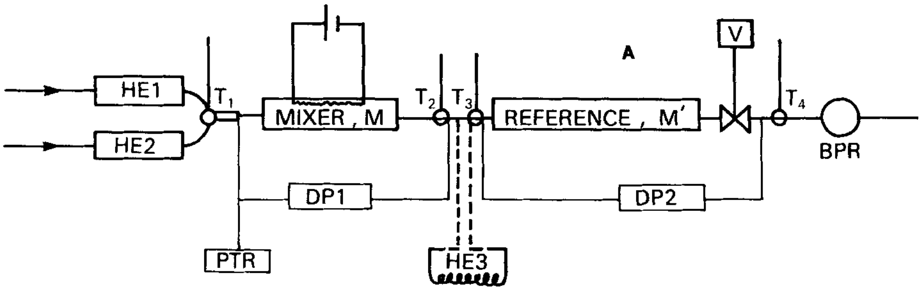

Figure 5a. Flow calorimeter.

HE1, HE2 Active heat exchangers
HE3 Heat exchanger
DP1, DP2 Differential pressure transducers
PTR Absoute pressure sensor
V Pressure regulating valve
BPR Back-pressure regulator
M' Reference flow circuit

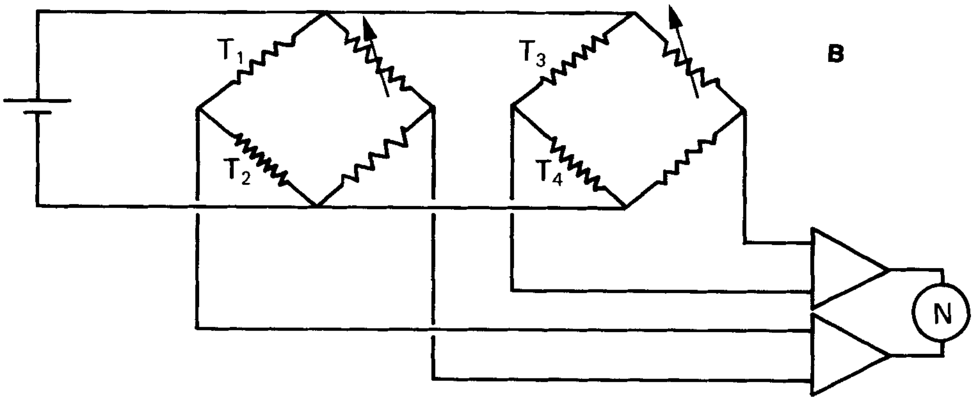

Figure 5b. Detector circuit.

T_1, T_2, T_3, T_4 Matched thermistors
N Null detector

in wires gave data with appreciable error. Reduction of loss through these conductive paths and more careful thermal isolation of the mixing and reference modules brought an immediate and considerable improvement. Conduction losses in lead-in wires have not received effective attention. A third-order ordinary differential equation governing steady state heat generation and conduction in a bimetal composite element with convective heat transfer to a surrounding fluid, derived by the authors, is solvable in principle but is of considerable complexity. Such detailed analysis is only desirable for heat capacity flow calorimetry where heat leaks (dependent on the property to be measured) constitute the principal practical problem. Our detailed analysis of this problem will be presented elsewhere. For excess enthalpy measurement it has been found sufficient to reduce heat leaks to very small values by the design discussed below.

Thermodynamic consistency testing

The most elementary test for thermodynamic consistency of measured h^E data is suggested by its temperature dependence at constant pressure:

$$\left(\frac{\partial h^E}{\partial T}\right)_p = C_p^E = C_{p_{mix}} - \sum x_i C_{pi}$$

which gives on integration:

$$h^E_{T_2} - h^E_{T_1} = \int_{T_1}^{T_2} C_{p_{mix}}\, dT - \sum \int_{T_1}^{T_2} x_i C_{pi}\, dT \quad (13)$$

The test suggested by Eq. 13 requires mixture heat capacity data seldom available, can only give information on the temperature dependence of measured h^E values at a given composition and, as with other area tests (e.g., for vapor-liquid equilibria), is a necessary but not sufficient condition for thermodynamic consistency. It nevertheless seems worthwhile to obtain mixture heat capacities from the same instrument measuring h^E data so as to perform the above test. The reference module of a flow calorimeter can be adapted to mixture heat capacity measurement, the principal difficulty being the elimination of flow-rate and physical-property-dependent heat leaks to the environment. The authors believe it is urgent that a more satisfactory, rigorous thermodynamic consistency test for excess enthalpy be developed and that future flow calorimeters be designed to provide the information necessary for consistency testing.

Equipment Description

Principle of operation

Our calorimeter design, incorporating the features analyzed above, is shown schematically with its detector circuit in Figure 5. The pure fluids are pumped through the heat exchangers HE1, HE2, reaching the entrance to the mixing section M at exactly equal temperatures. After complete mixing the homogeneous fluid is brought back to the original temperature by use of the passive heat exchanger HE3 and flows through the reference module M′. This is similar to M but has a shorter flow path to ensure a somewhat lower pressure drop. Fluid exiting from the

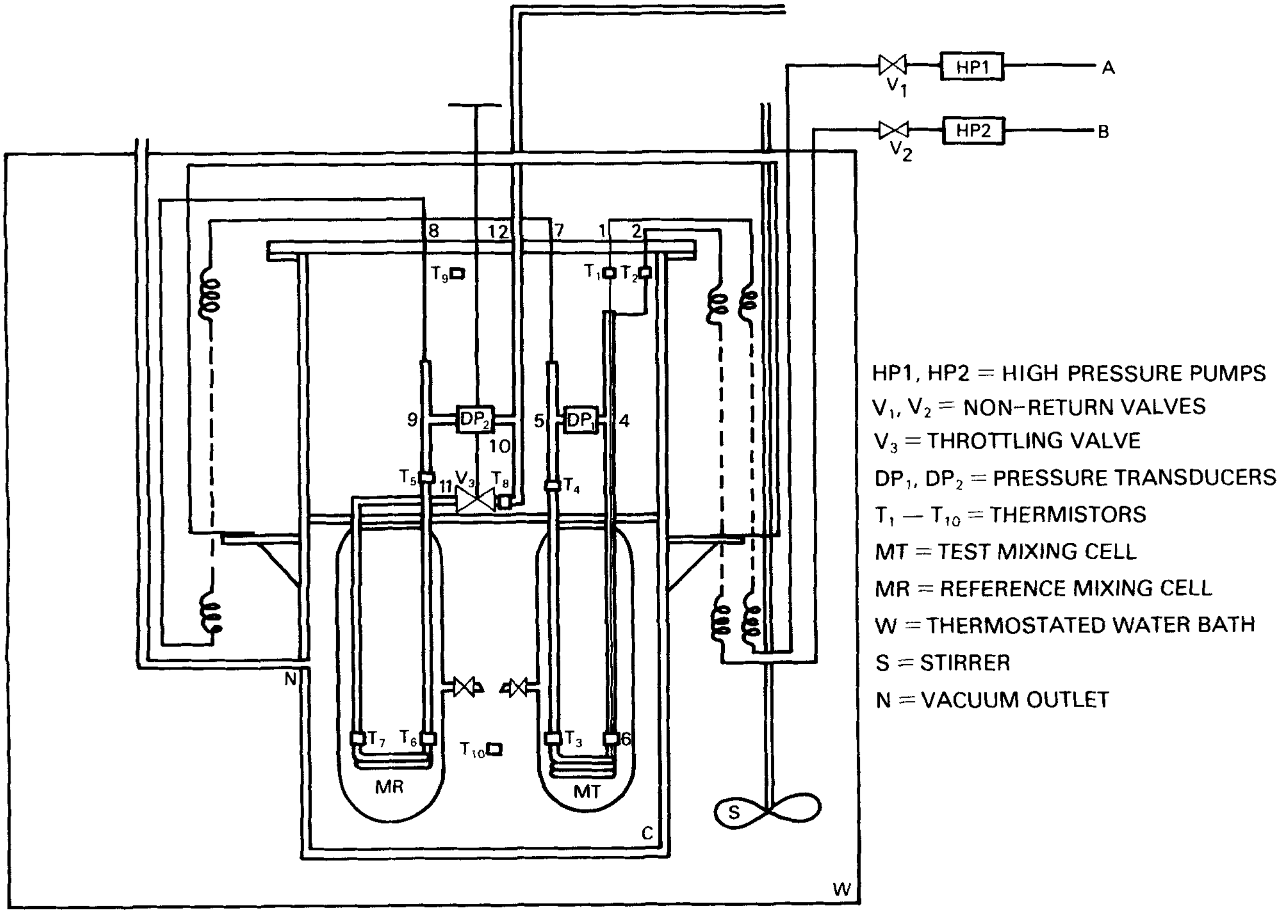

Figure 6. Calorimeter details.

reference module flows through the thermally insulated remote controlled throttling valve V and thence to the back-pressure regulator BPR.

Two sensitive wet/wet differential pressure transducers DP1, DP2 permit pressure drop monitoring and adjustment through valve V according to Eq. 8. The thermistors T1 to T4 installed in the flow path form elements of two Wheatstones bridges as shown in Figure 5b. The diagonal voltages are subtracted in a high-impedance device, which produces a null signal at N. This electrical subtraction is physically equivalent to subtracting temperature effects (friction, heat leaks, thermistor self-heating) in the reference module from those occurring in the test module. The null signal drives the direct current heating input to the mixing module and should therefore be independent of fluid flow rates and system physical properties and should respond only to the excess enthalpy.

Equipment details

The calorimeter details are shown in Figure 6. The two liquids, *A*, *B*, are pumped to the calorimeter with Beckman 110A high-pressure solvent metering pumps HP1, HP2 through pulse dampeners of our own design (not shown). The liquids are temperature-preequilibrated by passing through 2 m coils of 1,588 mm OD (0.4 mm ID) type 316 stainless steel tubing immersed in the temperature-controlled water bath W. These lengths were found experimentally (and can be predicted from Figure 2) to be adequate at all flow rates for the systems used to ensure precise temperature preequilibration.

The reference and mixing modules were contained in glass vessels evacuated to 0.4 kPa, and could be disassembled by means of B55 quickfit joints.

Fluids entered the glass cells through B5 Kovar graded metal seals, and a third Kovar seal was used as an electrical connector for the thermistor leads. The mixing tube and a similar but shorter tube in the reference cell were made from a 3.175 mm OD (1.588 mm ID), 0.86 m long Teflon tube containing a 27.23 Ω flat nichrome ribbon (0.05 × 0.8 mm) twisted into short alternating left- and righthanded helical elements similar to those of a Kenics static mixer. An important feature of the nichrome heating element was the connection to 0.15 mm copper wire closely coiled for at least 10 mm, as shown in Figure 7, at each connecting end and extending inside the tube along the fluid flow paths for an appreciable distance. This feature is believed to considerably reduce conduction heat losses through the lead-in wires. Connections are made through soldered points on the Kovar metal seals.

The Teflon mixing tubes were connected to glass tubes from the metal seals via Omnifit 1001 fittings with Teflon cone inserts to eliminate dead volume spaces. The Omnifit connectors permitted easy disassembly, e.g., to interchange different lengths of mixing tube, and served as thermal insulators in the fluid flow path. The fluids to be mixed are brought together after cocurrent flow for some distance, with fluid *A* injected into fluid *B* through a hypodermic syringe needle, Figure 7.

The thermistors T_1 to T_8 were housed in Teflon tubes fitted into the third leg of Omnifit T-pieces or into special Teflon housings, with the thermistor bead exposed directly to the flowing fluid in all cases. Yellow Springs models YSI 427 and YSI 46044 ("Super stable," installed later) were used and had nominal resistances of 2,250 and 5,000 Ω at 25°C respectively.

The Sensotec RDP P30 differential pressure transducers were connected as shown in Figure 6 via small-diameter Teflon tubes for thermal isolation from the flow path. Sensitivity was better than 0.13 kPa, although a long-term drift of 0.26 kPa was experienced for the reference cell transducer.

The two calorimeter modules were housed in an enclosed Perspex cylinder immersed in a constant-temperature bath controlled by a Braun Thermomix 1480 thermostat. The miniature throttling valve V was machined from Teflon with a short stainless steel needle thermally isolated from the control handle.

The calorimeter design described above was the result of considerable experimentation, particularly with the mixing module.

Electrical system

Matched thermistors T_1 and T_3, and T_6 and T_8 formed two arms of the test and reference Wheatstone bridges and are shown as R_1, R_2 and R_6, R_5, respectively, in Figure 8. The two diagonal voltages were isolated and fed to two type 741 operational amplifiers in series, which in turn subtracted the signals and inverted the net signal. The null output signal, which reflected temperature imbalances between reference and test sections of the calorimeter, were monitored with a Lloyd PL 2000 plotter or G32 galvanometer. The latter had a detectability of <1 μv, which gave a theoretical temperature resolution of 7×10^{-5}°C. Electrical heat input to the mixing section, measured on a Fluke multimeter, was from a constant-current DC supply. The two bridges were powered from a single highly stabilized power supply of our own design.

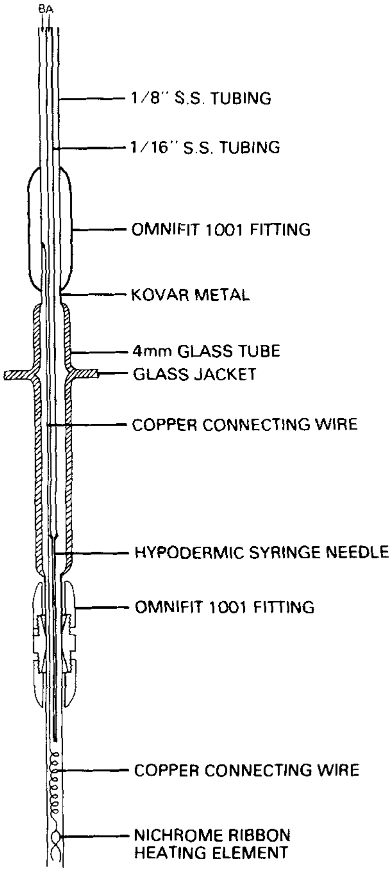

Figure 7. Liquid flow paths prior to mixing.

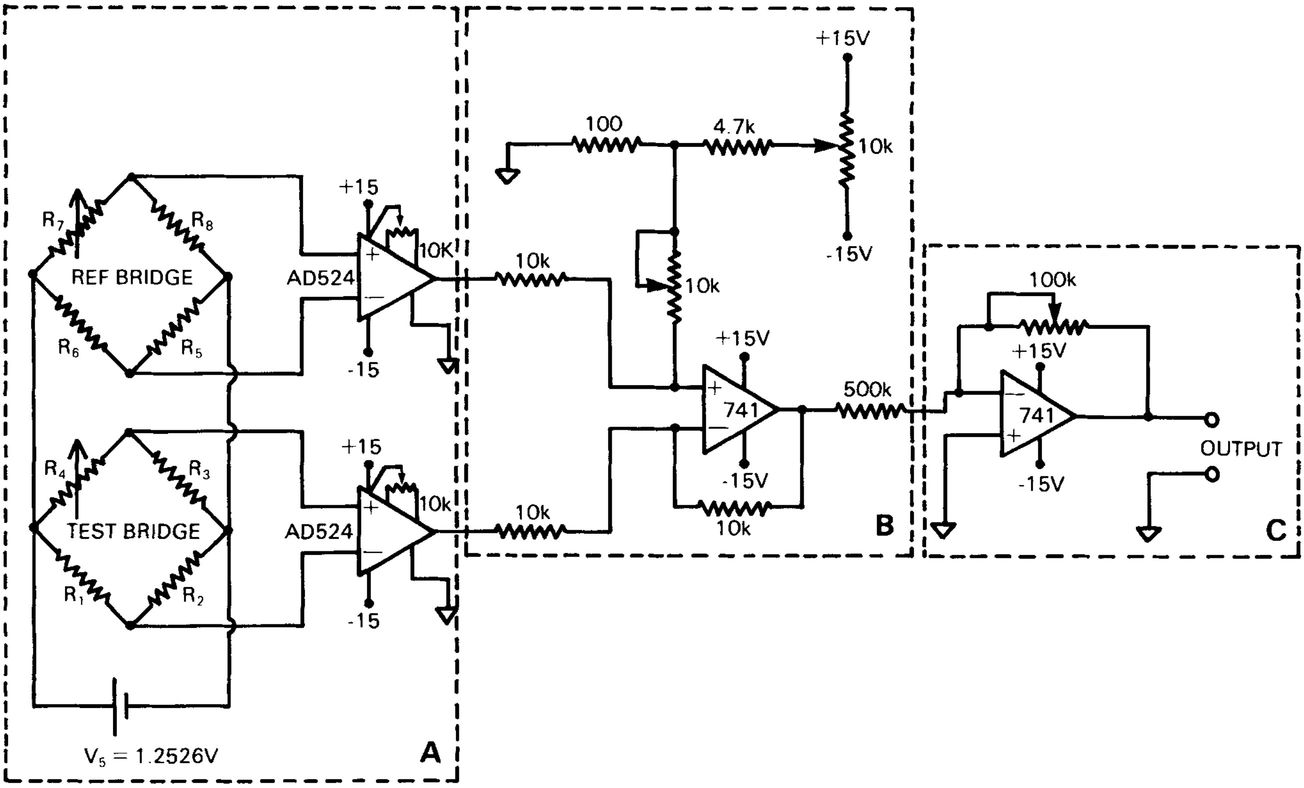

Figure 8. Electrical circuits.

A Bridge thermistors and signal isolation
B Subtractor and zero
C Inverter and gain

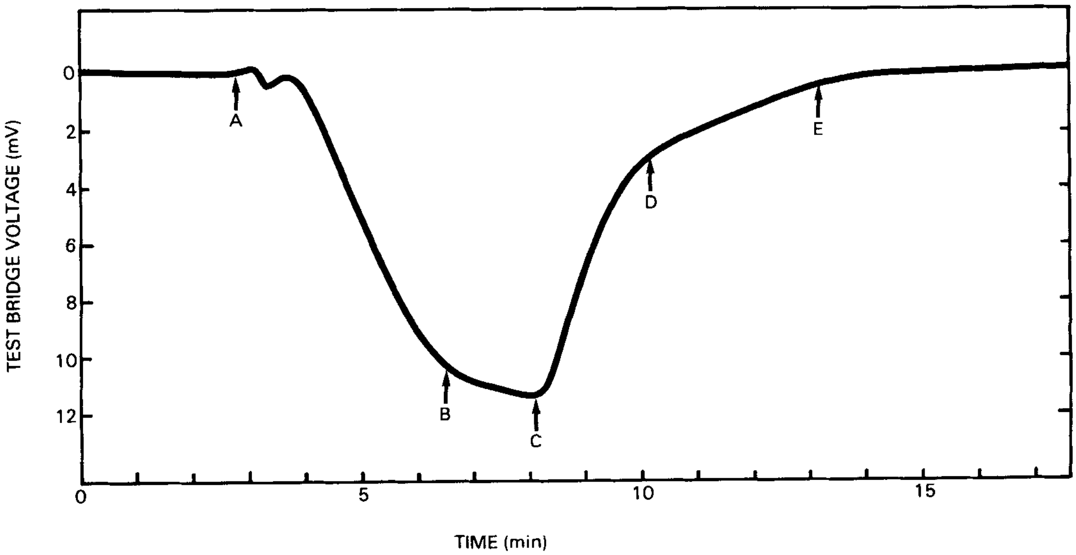

Figure 9. A typical heat-of-mixing run for cyclohexane–*n*-hexane at 25°C.

A Add cyclohexane at 1 mL/min to *n*-hexane at 6 mL/min
B Start adding heat; current = 30 mA
C Increase current to 80 mA
D Decrease current to 65 mA
E Decrease current to 58 mA

Measurement procedure

Measurements were started with a flow rate (usually 7 mL/min) of one pure fluid. The throttling valve was adjusted to give equal pressure drops (assuming $V \gg FV^E$) and the two bridges were zeroed. Fluid flow rates were then adjusted incrementally (e.g., 0.10 mL/min) to maintain the same volumetric flow rate and to cover the complete composition range. After each flow rate change the throttle valve was adjusted to maintain equal pressure drops and energy was supplied to the mixer to restore the null (difference) signal to its previous zero value.

Fluid flow rates $\dot{m}_1$, $\dot{m}_2$ were obtained from the pump digital settings and precise pump calibration charts (these were found to be fluid-specific). The mole fractions $\dot{m}_i/\Sigma\dot{m}_i$ were checked by refractive index analysis of the exiting fluid and excellent agreement was always found. The time required for a single measurement—a plotter trace for which is shown in Figure 9—was typically 10 min, and a complete data set for a binary mixture required about 2 h.

Results and Discussion

Hexane-cyclohexane system

Excess enthalpies were measured at 25°C over the complete composition range for the binary systems cyclohexane–*n*-hexane and cyclohexane–1-hexanol. The former, a nonviscous system, has recently been recommended by the IUPAC Commission on Thermodynamics and Thermochemistry (1970) for checking calorimeter data, since results for this system obtained in five different laboratories with batch, dilution, and flow calorimeters showed no systematic discrepancies. The recommended equation is:

$$h^E(\text{J/mole}) = x(1 - x)[866.10 - 249.4(1 - x) + 97.0(1 - x)^2 - 31.8(1 - x)^3] \quad (14)$$

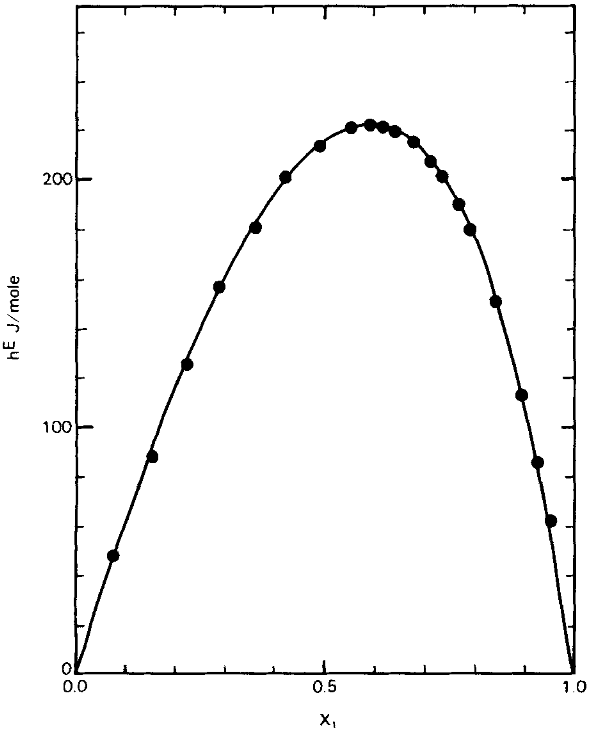

Figure 10. Excess enthalpies of binary cyclohexane (1)–*n*-hexane (2) at 298.15 K.

● Present data
—— Smoothed data set of Marsh and Stokes (1969)

Measured data for the hexane-cyclohexane system are shown in Figure 10 and Table 2. Chemicals from commercial sources of better than 99.5% purity were used without further purification. It is evident from Figure 10 that the present data set is in excellent agreement over the entire composition range with the very precise and accurate data of Marsh and Stokes (1969), which differ from Eq. 14 by no more than 0.53 J/gmol.

In Table 3 the data from our calorimeter are compared with other data sets from the literature for cyclohexane–*n*-hexane. Our data are surpassed in accuracy only by those of Marsh and Stokes and are superior to the batch calorimeter data of Mattingley et al. (1975). The data set of Grolier et al. (1975) obtained with a Picker flow calorimeter exhibits less scatter but has a substantially larger, systematic deviation from Eq. 14. The present data set is superior in precision and accuracy to those of Siddiqi and Lucas (1982) and McGlashan and Stoeckli (1969). In judging the precision, the various data sets were fitted to an equation of the following form by regression techniques:

$$h^E = x(1 - x)[A + B(1 - 2x) + C(1 - 2x)^2 + D(1 - 2x)^3] \quad (15)$$

The accuracy and precision of the present data set could probably be improved with better water-bath temperature control.

Table 2. Excess Enthalpies for Cyclohexane–*n*-Hexane at 25.0°C

Mol Frac. Cyclohexane	Excess Enthalpy Exper. J/mol	Residual* J/mol	Literature** J/mol	Residual† J/mol
0.0737	48.01	−0.70	48.08	0.07
0.1448	88.43	0.64	89.96	1.53
0.2144	125.48	0.01	126.22	0.74
0.2824	156.68	−0.44	156.71	0.03
0.3490	180.80	0.44	181.48	0.68
0.4144	200.43	−0.03	200.47	0.04
0.4784	213.29	0.21	213.48	0.19
0.5411	220.66	−0.30	220.32	−0.34
0.5780	221.80	−0.41	221.35	−0.45
0.6023	220.68	0.07	220.72	0.04
0.6264	219.05	−0.02	219.01	−0.04
0.6621	214.47	−0.09	214.38	−0.09
0.6972	207.22	−0.02	207.21	−0.01
0.7203	200.68	0.29	200.97	0.29
0.7545	189.45	−0.17	189.37	−0.17
0.7770	179.43	0.68	180.11	0.68
0.8328	150.85	0.20	151.00	0.15
0.8880	113.16	−0.40	112.67	−0.49
0.9217	85.34	−1.20	84.04	−1.30
0.9442	61.60	1.01	62.51	0.91

*h^E(correlating eq.) − h^E(exper.)
**h^E(eq. 14)
†h^E(eq. 14) − h^E(exper.)

Table 3. Statistical Comparison of Data Sets for Cyclohexane-*n*-Hexane at 25°C

Data Set	Precision: Avg. Std. Dev.* J/mol	Precision: Avg. Abs. Dev.* J/mol	Accuracy: Max. Abs. Dev.† J/mol	Accuracy: Avg. Abs. Dev.† J/mol	Type of Dev.
		Flow-type Calorimeter			
Present data	0.55	0.37	1.53	0.41	Random
Siddiqi & Lucas (1982)	0.78	0.71	2.23	1.17	Systematic
Grolier et al. (1975)	0.35	0.24	3.75	1.64	Systematic
Tanaka et al. (1975)	0.29	0.23	1.26	0.42	Random
McGlashan & Stoeckli (1969)	1.09	0.72	2.48	0.76	Random
		Batch-type Calorimeter			
Mattingley et al. (1975)	2.32	1.42	3.89	1.42	Random
Marsh & Stokes (1969)	0.09	0.07	0.53	0.19	Systematic

*With respect to Eq. 15
†With respect to Eq. 14

The latter was found to have a long-term drift of 0.01°C and a short-term fluctuation of 0.005°C.

Cyclohexane-1-hexanol system

This system has a much larger average viscosity ($\mu_{cyclohexane}$ = 0.88 × 10^{-3} Pa · s, $\mu_{hexanol}$ = 4.29 × 10^{-3} Pa · s) and was chosen to demonstrate the ability of the differential calorimeter to eliminate frictional heating. The data obtained are shown in Table 4 and are compared with the only two other existing data sets in Figure 11—those of Veseley and Pick (1969) and Nunez et al. (1976). The former workers used a batch U-tube calorimeter that was a modification of the design developed by Scatchard et al. (1952), whereas the Nunez et al. measurements were made with a Tian-Calvet batch calorimeter. Both published data sets differ substantially from the present one. To estimate the precision of the three data sets, regressions were attempted with an equation of the form of Eq. 15. This functional form was found

Table 4. Excess Enthalpies for Cyclohexane-1-Hexanol at 25°C

Mol Frac. Cyclohexane	Excess Enthalpy: Exper. J/mol	Excess Enthalpy: Smoothed* J/mol	Excess Enthalpy: Residual† J/mol
0.9845	192.20	192.53	0.37
0.9696	260.99	261.49	−0.50
0.9537	307.72	308.12	−0.40
0.9231	376.34	374.81	1.53
0.8925	423.49	424.67	−1.18
0.8466	489.39	487.01	−0.62
0.8006	538.92	536.28	2.65
0.7698	560.32	562.59	−2.27
0.7387	595.52	584.29	11.23
0.6918	609.18	608.55	0.64
0.6443	623.95	623.76	0.19
0.6123	628.68	628.05	0.63
0.5799	624.18	626.75	−2.57
0.5308	615.71	612.57	3.14
0.4810	582.04	581.79	0.25
0.4474	550.72	555.06	−4.34
0.4134	525.52	524.98	0.54
0.3620	477.21	474.21	3.00
0.3099	416.54	416.96	−0.42
0.2747	374.76	375.38	−0.62
0.2393	331.22	331.50	−0.28
0.1854	263.45	261.29	2.16
0.1309	184.31	188.92	−2.61
0.0941	134.53	135.26	−0.73
0.0568	83.74	82.03	1.71

*Calculated from a least-squares cubic spline regression
†h^E(exper.) − h^E(smooth)

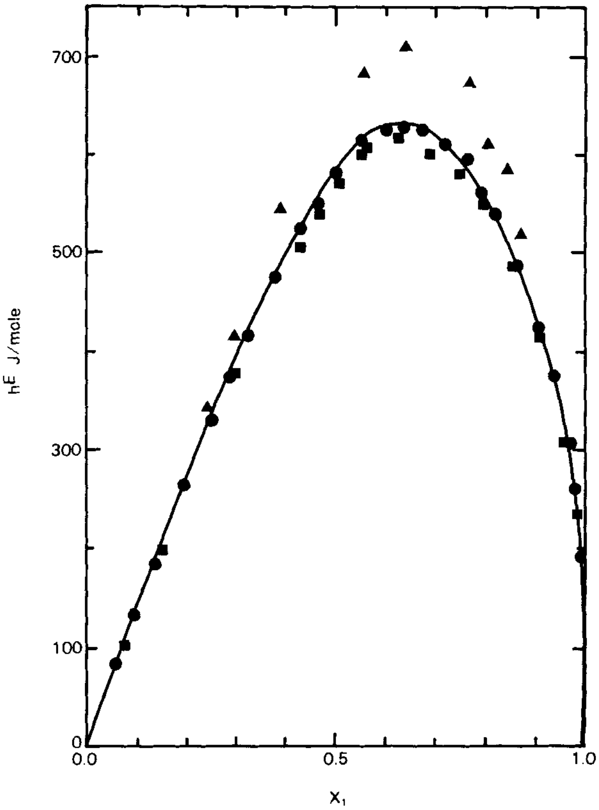

Figure 11. Excess enthalpies of binary cyclohexane (1)-1-hexanol (2) at 298.15 K.

● Present data
■ Data of Veseley and Pick (1969)
▲ Data of Nunez et al. (1976)

Table 5. Statistical Comparison of Data Sets for Cyclohexane–1-Hexanol at 25°C

Data Set	Std. Dev. J/mol	Avg. Abs. Dev. J/mol	Max. Abs. Dev. J/mol
Flow-type Calorimeter			
Present data	3.54	2.14	7.17
	(2.02)	(1.42)	(4.32)
Batch-type Calorimeter			
Nunez et al. (1976)	10.39	4.45	155.6
Veseley & Pick (1969)	5.64	4.19	8.76

Deviations in ( ) obtained using cubic spline regressions with six mol frac. intervals.

to be incapable of representing data for this system even when polynominals of successively higher order were used. A substantial improvement was obtained with a polynominal form incorporating a skewness factor, k:

$$h^E = \frac{x(1-x)[A + B(1-2x) + C(1-2x)^2 + D(1-2x)^3 + E(1-2x)^4]}{1 - k(1-2x)} \quad (16)$$

The results, using a Nelder-Mead regression procedure, are shown in Table 5 and confirm the superior precision of the present data set. A further improvement in fit was obtained using cubic spline regressions with six mole fraction intervals; these are shown in brackets for the present data set. The average absolute deviation (1.42 J/gmol) for our data set corresponds to 0.42% of the measured values and is in good agreement with that for the hexane-cyclohexane system (0.38%); i.e., the precision of the data for the much more viscous system is comparable to that for the nonviscous system.

In view of the presence of several potential sources of error in the equipment of Veseley and Pick (presence of small vapor spaces, nonreproducibility of stirring by tube rotation; heat capacities of tube mercury and mixed liquids), the very imprecise data of Nunez et al., and the ability of the present calorimeter to account for changes in system properties, we believe the present data set to be the best available for this system at 25°C.

To test the effect of viscous heating on the calorimeter response experiments were performed with pure 1-hexanol at varying flow rates. The effectiveness of pressure drop control with the throttling valve is demonstrated in Figure 12 where the difference (i.e., net) bridge voltages, measured before and after valve adjustment, are shown as a function of 1-hexanol flow rate over a sixfold flow rate variation. Apart from small random fluctuations, the net bridge signal is independent of flow rate. Since the net bridge signal controls the electrical energy input to the mixer, the calorimeter operation is seen to be flow-rate independent, a feature not present in any other flow calorimeter.

Conclusion

By incorporating the design guidelines developed for isothermal flow calorimeters and, particularly, a differential mode of operation based on an analysis of entropy generation in flows with mixing and friction, an instrument has been developed for accurate measurement of excess enthalpy for a wide range of liquids that mix endothermically. The lack of dependence of the measurement on flow rate and system physical properties, particularly viscosity, is believed to present a major advance in the field of calorimetry.

The calorimeter has a rapid response and yields results of an accuracy similar to those of the best flow calorimeters presently in use for inviscid systems and superior to those of some batch instruments. The ability of the instrument to compensate for frictional heating suggests that the results obtained for viscous systems will be superior to those obtained with other flow calorimeters.

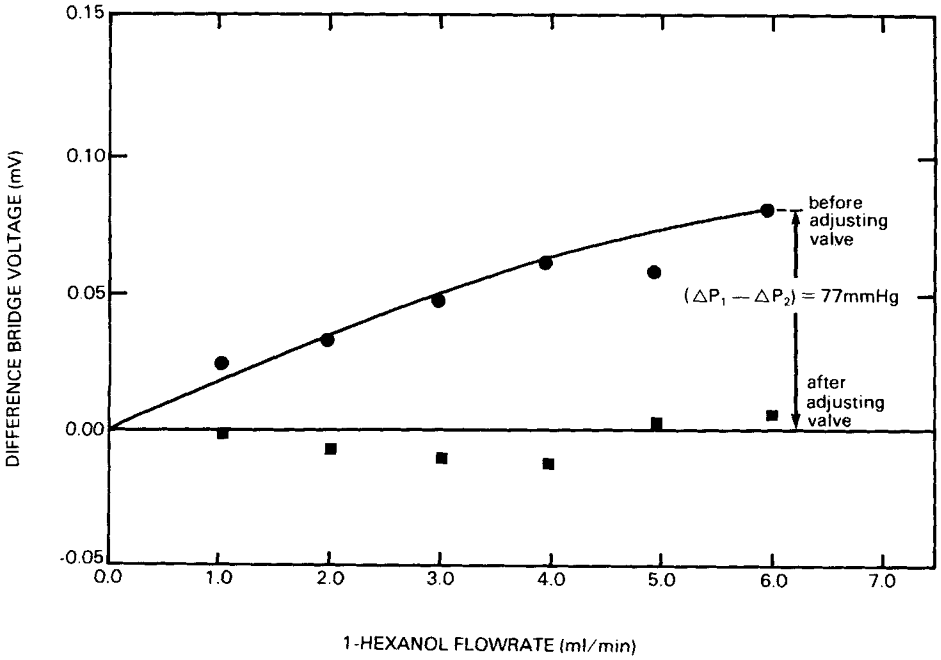

Figure 12. Effect of heating due to friction on difference bridge voltage.

Where unusually accurate data are required for viscous systems, e.g., for the testing of new thermodynamic theory, further small corrections for pressure drop and temperature rise can be incorporated in the instrument by calculation or design based on the equations developed for flows with friction and mixing. This will require evaluation of the ease-of-mixing factor F (neglected in this work), measurement of the mixture heat capacity, preferably in the instrument reference module, and knowledge of the system excess volume. Such further refinement poses a considerable challenge to researchers.

Acknowledgment

The authors are grateful for the generous financial aid received for this work from the CSP division of the Council for Scientific and Industrial Research

Notation

A = heat transfer area or component of binary mixture AB
C = thermal capacity $\dot{m}C_p$, W/K
C_p = constant pressure heat capacity, J/kg · K
C_p^E = excess heat capacity
D_i = tube inside diameter, m
D_j = bath inside diameter, m
D_H = diameter of tube coil, m
F = ease-of-mixing factor
g = gravitational acceleration, m/s^2
g^E = excess Gibb's free energy, J/kg
h = enthalpy, J/kg
h^E = excess enthalpy, J/kg
h_i, h_c = heat transfer coefficients, W/m^2 · K
I_s = intensity of segregation
k = thermal conductivity, W/m · K, or skewness factor (dimensionless) in Eq. 16
L = paddle length, Eq. 2, or tube length, Figure 2, m
ℓw_f = work lost to friction, frictional energy loss, Eqs. 6, 7
$\dot{m}$ = mass or molar flow rate, kg/s or kmol/s
N = paddle stirring rate, s^{-1}
p = pressure, Pa
Q = heat transfer rate, W
s = entropy, J/kg · K
$\dot{S}_{gen}$ = entropy generation rate, W/K
T = temperature, K
U = overall heat transfer coefficient, W/m^2 · K
u_b = bulk average velocity, m/s
V_1, V_2 = fluid specific volumes, m^3/kg
V^E = excess volume, m^3/kg
$\dot{V}$ = flow rate in Figure 2, cm^3/min
x_i = mole fraction of component i
z = height above datum line, m

Greek letters

α = thermal diffusivity, m^2/s
ϵ = heat exchanger effectiveness
ρ = fluid density, kg/m^3
μ = fluid viscosity, kg/m · s
μ_w = viscosity at wall temperature, kg/m · s

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Manuscript received Sept. 27, 1985, and revision received Oct. 6, 1986.