Separation of Fluid Frictional Energy and Heats-of-Mixing in a Flow Calorimeter

J. D. Raal
Dept. of Chemical Engineering, University of Natal, Durban 4001, South Africa

In an earlier article (Raal and Webley, 1987), a heat-of-mixing flow calorimeter design was described, in which a key feature was the ability to separate the desired excess enthalpy from fluid frictional effects, unavoidable in a flow calorimeter. Thorough mixing of fluids along the flow path necessarily entails a pressure drop which becomes particularly serious if one or both fluids is viscous.

In our earlier work, working equations were given for frictional energy loss in the measurement and reference arms of a flow calorimeter and for the respective temperature rises due to friction (Eqs. 6, 7, 9 and 10 of the earlier work). As a starting point, the macroscopic energy and entropy balances for an open system were given, and the derivational paths were briefly sketched. The derivation of Eqs. 6 to 10, however, is not obvious and requires a fair amount of detailed work. The derivations are given in detail below. Also, examples are given to illustrate the errors arising from fluid friction in a flow calorimeter.

A flow calorimeter with mixing and reference modules in series is shown in Figure 1. Pure fluids A and B enter at exactly equal temperatures and pressures T_1, p_1. Mixing is complete at the mixer exit, with temperature rise to T_2 and pressure drop to p_2. It is assumed that exactly sufficient electrical energy, Q, is added to compensate for the excess enthalpy of mixing, h^E.

The steady-state macroscopic energy and entropy balances for an open system apply:

$$\sum_{\text{in}} \dot{m}(h+U_b^2/2+gz)-\sum_{\text{out}} \dot{m}(h+U_b^2/2+gz)+\dot{Q}=0 \qquad (1)$$

$$\dot{S}_{\text{gen}}=\sum_{\text{out}} \dot{m}S-\sum_{\text{in}} \dot{m}S-\frac{\dot{Q}}{T} \qquad (2)$$

The second and third terms in the summation in Eq. 1 are kinetic and potential energies whose differences are assumed negligible across each calorimeter section. *KE* and *PE* changes can in any case be easily eliminated by experimental design.

The sequence of mixing and frictional energy loss in a flow calorimeter cannot be predicted, but two limiting cases can be defined. In the first, mixing is completed *before* frictional effects are manifested ("easy to mix systems"), and the pressure drop is due to the flow of the fully mixed solution. In the second case (difficult-to-mix fluids), the pure unmixed fluids experience a frictional pressure drop in cocurrent flow and a corresponding temperature rise to T_2 *before* mixing. The pressure drop and temperature rise equations for these two cases are derived as follows:

Case a: Easy-to-Mix Systems

The excess enthalpy is properly defined at T_1, p_1:

$$\dot{m}h^E=\dot{m}h_{AB}-\dot{m}_1h_A-\dot{m}_2h_B \qquad (3)$$

where subscript AB is a homogeneous mixture.

From Eq. 1 neglecting *PE*, *KE* changes for the mixing section:

$$\dot{m}_1h_A+\dot{m}_2h_B-\dot{m}h_{AB_2}+\dot{Q}=0 \qquad (4)$$

The enthalpy of the exit mixture at T_2, p_2 (h_{AB}) may be related to its value at T_1, p_1 by postulating a path in which the pressure is reduced to p_2 at constant temperature T_1 and the temperature increased to T_2 at constant pressure p_2:

$$h_{AB})_{T_2,p_2}=h_{AB})_{T_1,p_1}+\int_{p_1}^{p_2}\left(\frac{\partial h}{\partial p}\right)_{T=T_1}dp+\int_{T_1}^{T_2}\left(\frac{\partial h}{\partial T}\right)_{p=p_2}dT$$

$$=h_{AB})_{T_1,p_1}+V_{AB}(1-\alpha_{AB_1}T_1)(p_2-p_1)+C_{p_{AB}}(T_2-T_1) \qquad (5)$$

Assuming $C_p \neq f(T)$, $\alpha\left[=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)\right]_p$ = volume expansivity $\neq f(p)$.

Combining Eqs. 4 and 5, and dropping the subscript AB gives:

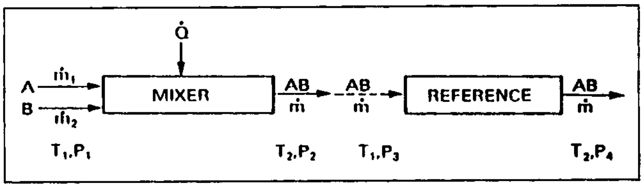

Figure 1. Mixing and reference sections.

$$\dot{Q} - \dot{m}h^E - \dot{m}\{C_p(T_2 - T_1) + V_1(1 - \alpha_1 T_1)(p_2 - p_1)\} = 0 \qquad (6)$$

Using a similar path for evaluating entropy change gives:

$$\int_1^2 dS = S_2 - S_1 = -\int_{p_1}^{p_2} (\alpha V)_{T=T_1} dp + \int_{T_1}^{T_2} \left(\frac{C_p}{T}\right)_{p=p_2} dT$$

that is,

$$S_{\text{out}} - S_{\text{in}} = C_p \ln\left(\frac{T_2}{T_1}\right) - V_1 \alpha_1 (p_2 - p_1) \qquad (7)$$

Substitution in Eq. 2 gives the entropy generation:

$$\dot{S}_{\text{gen}} = \dot{m}\left\{S_1^E + C_p \ln\frac{T_2}{T_1} - V_1\alpha_1(p_2 - p_1)\right\} - \frac{\dot{Q}}{T_1} \qquad (8)$$

Elimination of $\dot{Q}$ between the enthalpy and entropy balances, Eqs. 6 and 8, and assuming heat to be absorbed at temperature T_1 (as in Eq. 8) gives:

$$\frac{T_1\dot{S}_{\text{gen}}}{\dot{m}} = T_1 S_1^E - h_1^E - V_1(p_2 - p_1) + T_1 C_p \ln\frac{T_2}{T_1} - C_p(T_2 - T_1) \qquad (9)$$

To obtain the entropy generated by friction alone, the entropy generated in isothermal mixing and that due to heat transfer must be subtracted from Eq. 9.

Entropy Generation in Mixing

One may anticipate that the entropy generated in isothermal, isobaric mixing at T_1, p_1 (visualizable as a frictionless diffusion process) would be reflected by the excess Gibbs free energy. This is easily confirmed by application of Eqs. 1 and 2 to this situation, when again sufficient external energy is supplied to ensure isothermality:

$$\dot{m}_1 h_A + \dot{m}_2 h_B - \dot{m} h_{AB} + \dot{Q} = 0 \qquad (1a)$$

that is,

$$-\dot{m}h^E + \dot{Q} = 0$$

$$\begin{aligned}\dot{S}_{\text{gen}} &= \dot{m}S_{AB} - \dot{m}_1 S_A - \dot{m}_2 S_B - \frac{\dot{Q}}{T_1} \\ &= \dot{m}S^E - \dot{Q}/T_1 \\ &= \dot{m}S^E - \frac{\dot{m}h^E}{T_1} \qquad [(1a)] \qquad (2a)\end{aligned}$$

Therefore,

$$T_1 \frac{\dot{S}_{\text{gen}}}{\dot{m}} = T_1 S^E - h^E = -g^E \qquad (10)$$

Thus, finally, the lost work due to friction alone is obtained from Eqs. 9 and 10 as:

$$lw_f = \frac{T_1\dot{S}_{\text{gen}}}{\dot{m}} (\text{J/kg}) = -V_1(p_2 - p_1) + T_1 C_p \ln\frac{T_2}{T_1} - C_p(T_2 - T_1) \qquad (11)$$

The lost work is proportional to the pressure drop, a result obtainable from application of the macroscopic mechanical energy balance for an isothermal system. The two temperature-dependent terms, however, require interpretation. Inspection shows that the algebraic sum of the two terms represents and exergy (available work) due to the small temperature rise of the homogeneous mixture from fluid friction. This may be made clearer by rewriting Eq. 11 as:

$$lw_f = -V_1(p_2 - p_1) - \{\Delta h - T\Delta S\}_{p=p_2} \qquad (11a)$$

For temperature rises of a fraction of a degree (due to friction), the exergy term is extremely small and tends to zero as $T_2 \rightarrow T_1$ much more rapidly than either the enthalpy or entropy term individually. For practical purposes, the frictional lost work may therefore be approximated by:

$$lw_f = \frac{T_1\dot{S}_{\text{gen}}}{\dot{m}} = -V_1(p_2 - p_1) \qquad (12)$$

Equating lw_f to $(T_1\dot{S}_{\text{gen}})/\dot{m}$ for the frictional portion of the mixer is in accordance with the Gouy-Stodola theorem (see, for example, Bejan, 1982), for adiabatic systems.

Although the temperature rises due to friction can be neglected in analyzing the lost work in the mixing and reference cells, they must nevertheless be taken into account in calorimeter design since the heat input to the mixer is usually regulated from temperature measurements. This is discussed further below.

Case b: Difficult-to-Mix Systems

Here it is assumed that the pure fluids A, B experience a frictional pressure drop and temperature rise before mixing, and the enthalpy and entropy changes are therefore those for the pure (unmixed) fluids. This behavior would be approached with difficult-to-mix systems, for example, where density and viscosity differences between two components are large. For this case, h^E is properly defined at temperature T_2. Following the same procedure as for case a, with subscripts A, B denoting pure-component properties, Eqs. 6 and 8 for this case now become:

$$\dot{Q} - \dot{m}h^E - \dot{m}(T_2 - T_1)\{C_{p_{AB}} - C_p^E\} - (p_2 - p_1)\{\dot{m}_1 V_{A2}(1 - \alpha_{A2} T_2) + \dot{m}_2 V_{B2}(1 - \alpha_{B2} T_2)\} = 0 \qquad (14)$$

and

$$\dot{S}_{\text{gen}} = \dot{m}S^E + \ln\frac{T_2}{T_1}\{\dot{m}_1 C_{p_A} + \dot{m}_2 C_{p_B}\} - \{\dot{m}_1 V_{A2}\alpha_{A2} + \dot{m}_2 V_{B2}\alpha_{B2}\} - \frac{\dot{Q}}{T_2} \qquad (15)$$

Elimination of $\dot{Q}$ between these two equations, as before, gives after some rearrangement and simplification:

$$T_2\frac{\dot{S}_{\text{gen}}}{\dot{m}} = -g^E + (C_{p_{AB}} - C_p^E)\left\{T_2 \ln\frac{T_2}{T_1} - (T_2 - T_1)\right\} - (p_2 - p_1)(V_{AB2} - V^E)$$

Subtracting the entropy generated by the mixing process, g^E, and that due to heat transfer and again dropping the subscript *AB* for convenience gives:

$$lw_f = \frac{T_2\dot{S}_{\text{gen}}}{\dot{m}} = (p_1 - p_2)\{V_2 - V^E\} + (C_p - C_p^E)\left\{T_2 \ln\frac{T_2}{T_1} - (T_2 - T_1)\right\} \quad (16)$$

where V^E = excess volume.

It has been assumed in this derivation that temperature and pressure are uniform over a cross section at the end of the frictional path in the mixer module, an assumption that may involve somewhat more approximation for the temperature than the pressure.

The term involving temperatures in Eq. 16 can again be neglected in estimating the lost work. It is interesting to note that the pressure drop term now contains the multiplier $(V - V^E)_{T=T_2}$:

$$lw_f \doteq (p_1 - p_2)\{V_2 - V^E\} \quad (17)$$

In practice, mixing and viscous flow dissipation should lie between the extremes of initially complete mixing followed by viscous dissipation and the reverse sequence, that is, 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:

$$lw_f = (p_1 - p_2)\{V - FV^E\} \quad (18)$$

The factor F, an "ease of mixing factor" 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, however, in principle be determined in pressure drop experiments with fluid mixtures, as discussed below, and characterizes the operation of the mixing section of a flow calorimeter.

For the reference module, it is assumed that fully mixed homogeneous fluid *AB* experiences a pressure drop and temperature rise from p_3, T_1 to p_4, T_2. Following the procedure described above or directly from a macroscopic energy balance with $g^E = 0$, one obtains:

$$lw_f = \frac{T_1\dot{S}_{\text{gen}}}{\dot{m}} = V_1(p_3 - p_4) + T_1 C_p \ln\frac{T_2}{T_1} - C_p(T_2 - T_1) \cong V_1(p_3 - p_4)$$

These derivations show that, depending on the magnitudes of V^E and the ease of mixing factor F, equal pressure drops in the mixing and reference arms of a flow calorimeter will not in general ensure equal viscous dissipation, that is, the pressure drop in two geometrically identical mixing and reference sections may differ appreciably, if $F > 0$. Equations 18, 17 and 12 are those given without detailed derivation in our earlier article (Raal and Webley, 1987).

Temperature Rises

Although temperature rises, due to friction, are generally small, electrical heat input to the mixing section, which forms the principal measurement, is usually regulated via temperature measurements from thermistors or thermocouples. In many flow calorimeters, friction effects are simply neglected and energy input is regulated to maintain isothermal operation. Analysis of the temperature rises, due to friction, in both the mixing and reference modules is the key to elimination of frictional effects in a flow calorimeter.

For exactly equal pressure drops in the mixing and reference sections of a flow calorimeter (a desirable mode of operation) and with energy input correctly equal to the excess enthalpy ($\dot{m}h^E = Q$) in the former section, the respective temperature rises due to friction, denoted by subscripts 1 and 2, respectively, are found directly from Eqs. 6 and 14. The result is:

Case a:

$$(T_2 - T_1)_1 = (T_2 - T_1)_2 \quad (19)$$

Case b:

$$\frac{(T_2 - T_1)_2}{(T_2 - T_1)_1} = \frac{V(1 - \alpha T_2)}{V(1 - \alpha T_2) - V^E(1 - \alpha^E T_2)}\,\frac{C_p - C_p^E}{C_p} = \frac{V'}{V' - V^E}\,\frac{C_p - C_p^E}{C_p} \quad (20)$$

Equation 20 was given as Eq. 10 in our earlier article. For incompressible liquids ($\alpha = 0$), $V' = V$.

In practice, the correction term in Eq. 20 may be generalized as:

$$\frac{\Delta T_2}{\Delta T_1} = \frac{1}{1 - \frac{FV^E}{V}}\left(1 - \frac{FC_p^E}{C_p}\right) \cong \left[1 - \frac{FC_p^E}{C_p}\right] \quad (21)$$

with $0 \le F \le 1$. This generalization, although not rigorous, is quite satisfactory for all practical purposes.

Calorimeter Operation

The results embodied in the above equations may be incorporated into calorimeter operation as follows. The simplest mode of operation is to adjust the pressure drop control valve to give equal pressure drops in the reference and measurement arms of the instrument (as was done in our experiments). This should first be done with one of the pure fluids and the pressure drops recorded for a given volumetric flow rate. For a mixture at the same total volumetric flow rate, the pressure drops should again be recorded and the valve adjusted to equalize the pressure drops. For easy-to-mix systems, $F \cong 0$, the pressure

Table 1. Calculation of Ease-of-Mixing Factors from Viscosity Data

System	Mole Fraction x_1	Viscosities (cp) μ_1	μ_2	μ_{soln}*	μ_{TP}**	μ_{expt}†	F $\left[= 1 - \left\lvert\frac{\mu_{expt} - \mu_{TP}}{\mu_{soln} - \mu_{TP}}\right\rvert\right]$
1-propanol(1)-	0.35			0.52	0.727	0.65	0.630
n-hexane(2)	0.35	2.12	0.294	0.52	0.727	0.55	0.146
	0.80			1.311	1.564	1.50	0.746
diethyleneglycol(1)	0.75			14.32	32.18	28	0.766
-benzene(2)		42	0.67	1.808			
	0.25				10.99	8.7	0.75

*From the Grunberg and Nissan equation, $\ln \mu_{soln} = x_1 \ln \mu_1 + x_2 \ln \mu_2 + x_1 x_2 G_{12}$ (G_{12} = structural interaction parameter). Refer to Reid et al., 1987).

** μ_{Tp} from Eq. 22.

† Values chosen for illustration, $\mu_{soln} < \mu_{expt} < \mu_{Tp}$.

drops and temperature rises should remain essentially equal in the two sections, although they may differ from the pure fluid values due to viscosity changes with composition.

With difficult-to-mix systems ($F \cong 1$) the temperature rise in the reference section will not be the same as that in the mixer section for equal pressure drops, but will be in accordance with Eq. 21. For accurate results with viscous systems, where frictional energy dissipation will be large, reasonably accurate values of factor F will be required. The complexity of two-phase flows, which may be manifested in six different flow regimes, makes a rigorous procedure for evaluating F difficult to devise. The following method is proposed as an illustration.

Determination of F

With the pressure-regulating valve at a setting which gives equal pressure drops with a pure fluid, measure the pressure drops when a mixture is pumped through at the same total volumetric flow. Let these observed pressure drops be $(-\Delta p)_{Expt}$ and $(-\Delta p)_{soln}$ for the mixing and reference modules, respectively. For difficult-to-mix systems, these readings should differ. The pressure drops are assumed to be related to the effective viscosity μ by:

$$-(\Delta p) = R_m \mu U_b,$$

where

R_m = resistance of fluid path (assumed invariant and found from the pressure drop for a pure fluid)

U_b = bulk average fluid velocity

Suppose the effective viscosity for a completely unmixed two-phase flow of components A and B, μ_{TP} is given by an equation such as that of Dukler et al. (1964) (See also Brodkey, 1967) for homogeneous flow:

$$\mu_{Tp} = \mu_A x_A + \mu_b x_b \quad (x = \text{volume fraction}) \tag{22}$$

A dimensionless measure of the difficulty of mixing is then:

Table 2. Temperature Rises Due to Friction and Corresponding Calorimeter Errors

	Heat Capacities at 20°C J/mol·K							Temp. Rise Due to Friction (°C)†			Est. Calorimeter Errors‡ J/mol	
System	C_{p_1}	C_{p_2}	x_1	$C_{p_{mix}}$	C_p^E**	F	$-\Delta p$*** (kPa)	Mixing Section ΔT_1	Ref. Section ΔT_{11}	$\Delta T_1 - \Delta T_{11}$	Without Reference Section	With Reference Section
1-propanol(1)-	143.6	195.2	0.35	190.2	13.1	0	6.23	0.0036	0.0036	0.0	0.69	0.0
n-hexane (2)						0.63	7.78	0.0049	0.0046	−0.0003	0.93	0.06
						1.0	8.71	0.0055	0.0051	−0.0004	1.05	0.07
			0.80	161.4	7.5	0	15.7	0.0084	0.0084	0.0	1.36	0.0
						0.746	17.97	0.0096	0.010	0.00049	1.55	0.08
						1.0	18.73	0.0105	0.010	0.00049	1.70	0.08
Diethylene-	229.2	131.8	0.25	157.5	58.6	0	6.69	0.0038	0.0038	0.0	0.61	0.0
glycol(1)-						0.75	98.3	0.0900	0.0565	0.0335	14.17	5.27
benzene (2)						1.0	124.1	0.1136	0.0713	0.0423	17.88	6.65
			0.75	214.3	9.4	0	161.7	0.0706	0.0706	0.0	15.12	0.0
						0.766	316.2	0.1380	0.1443	0.0063	30.92	1.36
						1.0	363.7	0.1587	0.1660	0.0073	35.57	1.56

*Computed from $C_{p_{mixt}} = C_p^E + \Sigma x_i C_{pi}$.

**Computed from $C_p^E = (\partial h^E/\partial T_p) \cong (\Delta h^E/\Delta T)$, h^E data from Christensen et al. (1982).

*** $-\Delta p = Rm\mu U_b$; using experimental values obtained with other pure fluids at 9.0 mL/min, taking Δp to be proportional to appropriate viscosity (from Table 1).

† $\Delta T_1 = \frac{(-\Delta P) V_{soln}}{C_{p_{mix}} - C_p^E}$, $\Delta T_2 = \frac{(-\Delta p) V_{soln}}{C_{p_{mix}}}$ from Eqs. 14 and 6 for cases b and a, respectively (for $\dot{m} h^E = \dot{q}$ and neglecting α and V^E).

‡ For calorimeters without a reference section, estimated error in $h^E \cong (\Delta T_1)\ (C_{p_{mix}})$. For calorimeters *with* a reference section and maintaining equal pressure drops, but not allowing for differences in $(\Delta T)s$, that is, neglecting the temperature correction term given with close approximation by Eq. 21, error in $h^E \cong (\Delta T_1 - \Delta T_2) C_{p_{mix}}$.

$$\frac{\mu_{\mathrm{Expt}}-\mu_{Tp}}{\mu_{\mathrm{soln}}-\mu_{Tp}}$$

where

μ_{soln} = viscosity of fully mixed solution of A and B
μ_{expt} = observed viscosity in mixing section

Thus,

$$F=1-\left|\frac{\mu_{\mathrm{expt}}-\mu_{Tp}}{\mu_{\mathrm{soln}}-\mu_{Tp}}\right| \qquad (23)$$

For easy-to-mix systems, μ_{expt} would approach μ_{soln} and $F\rightarrow 0$. For difficult-to-mix systems, μ_{expt} approaches μ_{Tp} and $F\rightarrow 1$.

With F known at each composition, Eq. 21 can be used in experimental runs for the h^E measurement. It is worth noting that, by experimental design, F can be made very small by having an efficient mixing device and a considerable mixer length.

For equal pressure drops in the two calorimeter sections (by valve adjustment) the temperature rises should be in accordance with Eq. 21.

The heat capacity of the solution C_p and the excess heat capacity:

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

can both be determined from the calorimeter without equipment modification. The twin Wheatstone bridges can be adjusted so that heat input readings are taken with temperatures (that is, resistances) in accordance with Eq. 21.

The procedure is admittedly complex and would be justifiable only when F is clearly nonzero and the system viscosity appreciable. Although tested so far only for relatively nonviscous systems, recent results (Raal and Naidoo, 1990) have shown that our calorimeter can give results rivaling the excellent batch calorimeter data of Marsh and Stokes (1969). Expected error magnitude is illustrated for two systems of widely differing viscosities in Tables 1 and 2.

It is evident from Table 2 that operating a flow calorimeter without a reference section can produce frictional errors ranging from appreciable to considerable depending on the viscosity of the mixture. Moreover, the error depends on both composition *and* the ease-of-mixing factor F. For relatively nonviscous systems, operating with a reference section and ensuring equal pressure drops should give excellent results. For highly viscous systems, such as the second system in the tables, accurate results (for $F\neq 0$) can be obtained only by determining F and allowing for the temperature rises in the two sections according to Eq. 24. The method of implementation will depend on the characteristics of the electronic circuit used to obtain a null signal from the two calorimeter sections.

Literature Cited

Bejan, A., *Entropy Generation through Heat and Fluid Flow*, Wiley, New York (1982).

Brodkey, S., *The Phenomena of Fluid Motions*, Addison-Wesley Publishing Co. (1967).

Christensen, J. J., R. M. Izatt, and R. W. Hanks, *Handbook of Heats-of-Mixing*, Wiley-Interscience, New York (1982).

Dukler, A. E., M. Wicks, and R. G. Cleveland, "Frictional Pressure Drop in Two-Phase Flow: an Approach through Similarity Analysis," *AIChE J.*, **10**, 44 (1964).

Marsh, K. N., and R. H. Stokes, "Enthalpies of Mixing of *n*-Hexane and Cyclohexane at 25°C," *J. Chem. Thermod.*, **1**, 223 (1969).

Raal, J. D., and P. A. Webley, "Microflow Calorimeter Design for Heats-of-Mixing," *AIChE J.*, **33**, 604 (1987).

Raal, J. D., and P. Naidoo, "Excess Enthalpy Measurements Using a Novel High Refined Microflow Calorimeter and the Prediction of Vapour-Liquid Equilibria from Such Data," *Fluid Phase Equilib.*, **57**, 147 (1990).

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, McGraw-Hill, New York (1988).

Manuscript received Sept. 26, 1991, and revision received Aug. 18, 1992.