Table IV. Error in Using Polynomial Expansion

	Average error		Maximum error	
Temp, °C	g^E, cal/mol	P, mm	g^E, cal/mol	P, mm
	Triethylamine-*n*-butyl alcohol			
10.0	0.16	0.03	0.39	0.08
20.05	0.46	0.13	1.30	0.47
30.05	0.16	0.08	0.31	0.19
40.0	0.23	0.15	0.44	0.38
	Triethylamine-sec-butyl alcohol			
10.0	0.26	0.05	0.64	0.12
20.05	0.34	0.09	0.78	0.23
30.05	0.30	0.13	0.71	0.34
40.0	0.47	0.27	0.93	0.60
	Triethylamine-tert-butyl alcohol			
25.0	0.27	0.09	0.78	0.25
30.05	0.18	0.12	0.57	0.22
40.0	0.28	0.20	2.26	0.39

Nomenclature

a_j = constants in Equation 3
f = fugacity
g^E = molar excess Gibbs free energy, cal/g-mol
P = total pressure, mm Hg
x = liquid mole fraction
y = vapor mole fraction

Greek Letters

γ = activity coefficient = $f/f^\circ x$
Φ = ratio of the fugacity coefficient of a pure component to the component fugacity coefficient in the mixture

Subscripts

1 = more volatile component or amine
2 = less volatile component or alcohol

Superscripts

$^\circ$ = pure component

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Enthalpies of Mixtures of Polar and Nonpolar Component: System *n*-Pentanol–*n*-Heptane

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Enthalpy data were measured for mixtures of *n*-pentanol and *n*-heptane containing 0.250, 0.500, and 0.750 mole fraction *n*-pentanol. The measurements covered the range from 100 to 1000 psia and 350–600°F and included the liquid, vapor, vapor-liquid, and critical regions. The experimental results in the vapor phase were compared with values calculated by two methods for prediction of variation of enthalpy with pressure, those of Lydersen and Storvick.

To test and develop methods for prediction of enthalpy of nonideal mixtures, direct enthalpy measurements were carried out for the *n*-pentanol–*n*-heptane system as a function of composition (0.250, 0.500, 0.750 mole fraction *n*-pentanol), temperature (350–600°F), and pressure (100–1000 psia). No generalized and adequate method for prediction of enthalpy of nonideal solutions is yet available (*7*).

For a few *n*-alcohol-hydrocarbon systems (benzene-methanol, benzene-ethanol, *n*-pentane-ethanol) McCracken et al. (*3*) and Storvick and Smith (*9–11*) have proposed a correlating procedure based upon association of the alcohol.

This paper presents enthalpy data as well as an evaluation of the methods for prediction of enthalpy of Lydersen et al. (*2*) and Yen and Alexander (*15*), and McCracken et al. (*3*) and Storvick and Smith (*9–11*).

Experimental

The flow calorimeter utilized in this work, as well as the experimental procedure followed, have been described previously (*12*). The *n*-pentanol and *n*-heptane used were from Fisher Scientific Co., respectively, of lot 716063, with a boiling range of 137.7–138.0°C, and lot 785040 with certified spectroanalysis. Evaluation of the apparatus performance with pure *n*-pentane has been discussed in the previous article (*12*), an error analysis indicating the overall possible error on the measured enthalpy values to be ±1.1 Btu/lbm. Enthalpy data for pure *n*-pentanol and *n*-heptane have been reported in previous work (*12, 13*).

Principles of Enthalpy Determinations

The enthalpy is determined by measuring the energy transferred from the test fluid to the boiling Freon-11. The enthalpy

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change ($\Delta H_c = H_2 - H_1$) between the thermodynamic states at the outlet and the inlet of the calorimeter can be calculated from the weight of Freon-11 evaporated (W_f), its latent heat of vaporization (L_f), and the mass of fluid sample collected during the run (W_c). Namely:

$$\Delta H_c = H_2 - H_1 = -L_f W_f / W_c \qquad (1)$$

Correction must be made to the ΔH_c values obtained from Equation 1 to refer the enthalpies to the desired reference state of H equal to 0, for the pure liquid components at 77°F and their vapor pressures.

Exit temperature correction. A small correction, Δh_1, usually about 1 Btu/lbm of mixture, is necessary to account for exit temperatures which were different from the desired 77°F reference temperature. This correction was performed by utilizing the mole fraction averages of the heat capacities for the pure liquid *n*-pentanol and *n*-heptane near 77°F, which were available in the literature (*1*). The order of magnitude of this approximate correction Δh_1 is, however, within the experimental error of this work. Introducing the exit temperature correction (Δh_1) into Equation 1 and rearranging yields:

$$(H_1 - H_2')_P = L_f W_f / W_c + \Delta h_1 \qquad (2)$$

The values of $(H_1 - H_2')_P$ represent the enthalpy differences between the inlet and datum temperature of 77°F, at the pressure (P) of the system.

Pressure correction on liquid enthalpy at 77°F. The values of H_1 and H_2' in Equation 2 correspond essentially to the same pressure, namely that at which the data are taken, since the pressure drop across the calorimeter is negligible. Since the pressure of the reference state is taken as the vapor pressures of the individual components at 77°F, a pressure correction, Δh_2, should be included in Equation 2. An approximate correlation for the isothermal effect of pressure on the enthalpy of pure liquids has been proposed by Watson (*14*). Calculations for the pure components used in this work indicated that at 1000 psia, the pressure corrections for pure *n*-pentanol and *n*-heptane are, respectively, about 2.2 and 3.3 Btu/lbm.

The value of this correction, Δh_2, for the mixtures studied is taken from the mole fraction averages of the pure component pressure corrections at the desired elevated pressure. Up to the critical pressure, the pressure correction Δh_2 is usually less than 1 Btu/lbm of mixture for all three mixtures studied and thus is within the experimental error of this work.

With Δh_2 designating the pressure correction, Equation 2 is rewritten as:

$$H_1 - H_{2vp}' = L_f W_f / W_c + \Delta h_1 + \Delta h_2 \qquad (3)$$

where H_{2vp}' is the enthalpy of the liquid mixture at 77°F and the vapor pressures of its pure components at this temperature.

Correction for heats of mixing. The pure component

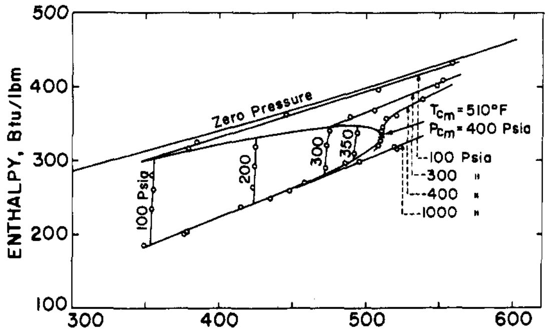

Figure 1. Temperature-enthalpy diagram for 25 mol % *n*-pentanol and 75 mol % *n*-heptane mixture. Datum: $H = 0$, pure liquid components at 77°F

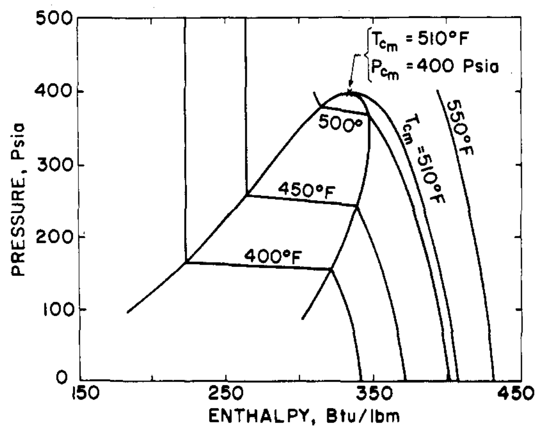

Figure 2. Pressure-enthalpy diagram for 25 mol % *n*-pentanol and 75 mol % *n*-heptane mixture. Datum: $H = 0$, pure liquid components at 77°F

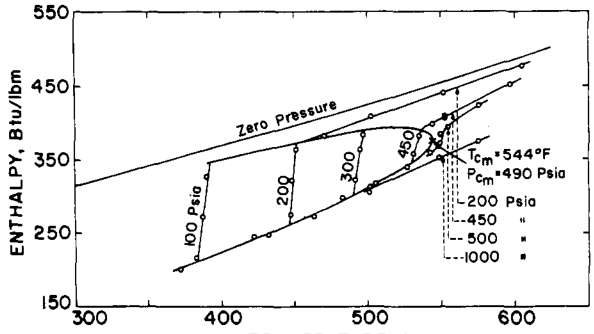

Figure 3. Temperature-enthalpy diagram for 50 mol % *n*-pentanol and 50 mol % *n*-heptane mixture. Datum: $H = 0$, pure liquid components at 77°F

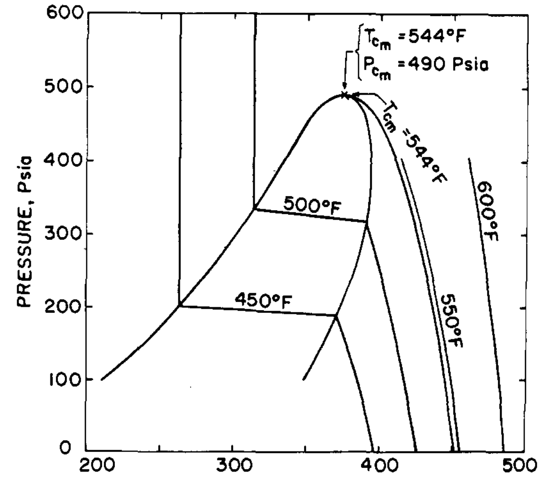

Figure 4. Pressure-enthalpy diagram for 50 mol % *n*-pentanol and 50 mol % *n*-heptane mixture. Datum: $H = 0$, pure liquid components at 77°F

enthalpies at 77°F and their vapor pressures are related to the enthalpy of the exit stream through the heat of mixing, ΔH_m°, by the expression:

$$H_{2vp}' = \Delta H_m^\circ + \sum_i x_i H_i^\circ \qquad (4)$$

The superscript zero refers to the reference state. The exit stream enthalpy referred to the reference state, H_{2vp}', is equal to the heat of mixing ΔH_m°, because the summation of $x_i H_i^\circ$ is zero by the definition of the reference state. Thus:

$$H_{2vp}' = \Delta H_m^\circ \qquad (5)$$

Introducing the correction ΔH_m° for the heat of mixing, Equation 3 becomes:

$$H_1 = L_f W_f / W_c + \Delta h_1 + \Delta h_2 + \Delta H_m^\circ \qquad (6)$$

Equation 6 is the expression for the enthalpy of the mixture corrected to the desired reference state before smoothing. The heats of mixing for the *n*-pentanol–*n*-heptane system were taken from the literature (*6*).

Experimental Results for *n*-Pentanol–*n*-Heptane System

From the isobaric lines constructed on a *H* vs. *T* chart, *P* vs. *H* charts were constructed by cross-plotting, with isotherms being drawn. These diagrams are shown in Figures 1–6 (only a sample of a few isobars and isotherms is shown in these figures). Figure 7 shows a comparison of the dew and bubble-point curves for the system *n*-pentanol–*n*-heptane at the three indicated compositions, the boiling point curves of the pure *n*-pentanol and *n*-heptane being also plotted in the same figure. A sample of the enthalpy data obtained is presented in Tables I–III. Extensive tabulation of the enthalpy data and large-scale enthalpy charts have been deposited with the ACS Microfilm Depository Service.

Plotting the *P* vs. *H* and *H* vs. *T* diagrams provided rough estimates of the critical pressures and temperatures. Once the enthalpy data were smoothed by cross-plotting the *P* vs. *H* and *H* vs. *T* diagrams, the phase envelope was obtained by drawing a smooth curve through the points of discontinuity on the temperature–enthalpy and pressure–enthalpy diagrams. The critical point lies approximately on the curve joining the midpoints of different vapor-liquid equilibrium lines drawn on a phase envelope (*8*). The precision of all the critical temperatures and pressures thus estimated is believed to be ±2°F and ±3 psi, respectively. Table IV presents the critical temperatures and pressures of the three mixtures studied, as estimated from the measurements along with those calculated by Kay's pseudocritical rules (*7*).

Comparison of Experimental Results with Predicted Values

Experimental results obtained in this work were compared with values calculated by two methods for prediction of variation of enthalpy with pressure, those of Lydersen et al. (*2*) and Yen and Alexander (*15*), and McCracken et al. (*3*) and

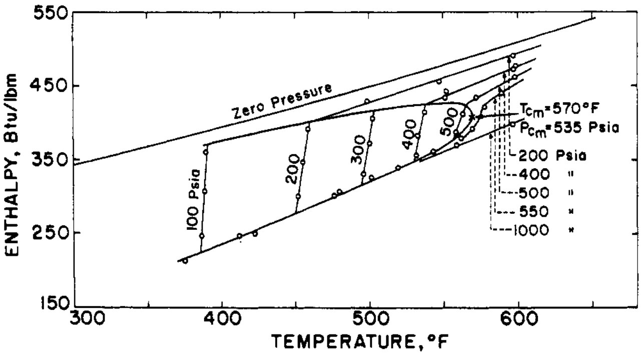

Figure 5. Temperature–enthalpy diagram for 75 mol % *n*-pentanol and 25 mol % *n*-heptane mixture. Datum: *H* = 0, pure liquid components at 77°F

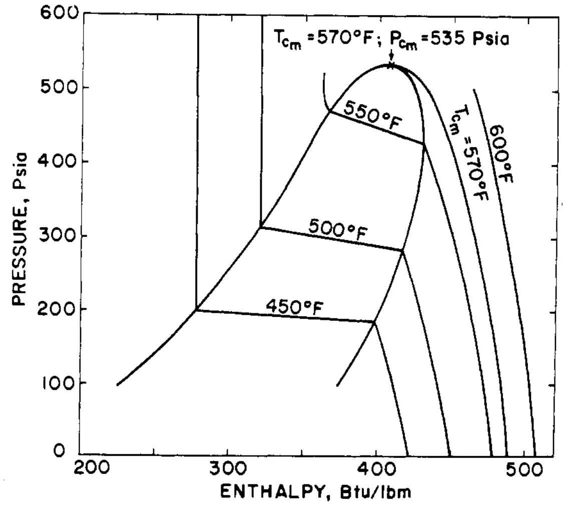

Figure 6. Pressure–enthalpy diagram for 75 mol % *n*-pentanol and 25 mol % *n*-heptane mixture. Datum: *H* = 0, pure liquid components at 77°F

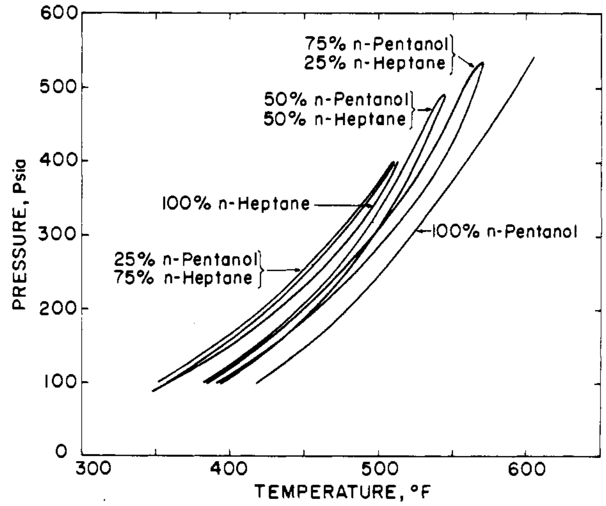

Figure 7. Comparison of dew and bubble-point curves for system *n*-pentanol–*n*-heptane at three indicated compositions

Table I. Sample of Enthalpy Data of 25 Mol % *n*-Pentanol and 75 Mol % *n*-Heptane Mixture

Reference state: *H* = 0, pure liquid components at 77°F

Press, psia	Temp, °F	*H*, Btu/lbm (from measurements)	*H*, Btu/lbm (smoothed)
100	345.5	182.0	180.5
	353.4	235.9	235.9
	355.1	260.1	260.1
	355.2	279.4	279.4
	379.8	318.6	319.5
	385.1	323.3	323.0
	445.7	361.5	360.0
	507.6	398.4	399.0
	547.4	425.3	424.0

Table II. Sample of Enthalpy Data of 50 Mol % *n*-Pentanol and 50 Mol % *n*-Heptane Mixture

Reference state: $H = 0$, pure liquid components at 77°F

Press, psia	Temp, °F	*H*, Btu/lbm (from measurements)	*H*, Btu/lbm (smoothed)
100	372.2	200.4	201.5
	381.6	215.1	215.1
	386.7	270.0	270.0
	390.8	327.2	327.2
	418.9	364.6	364.0
	474.6	397.8	400.0
	547.0	447.0	446.5
	598.1	479.3	479.0

Table III. Sample of Enthalpy Data of 75 Mol % *n*-Pentanol and 25 Mol % *n*-Heptane Mixture

Reference state: $H = 0$, pure liquid components at 77°F

Press, psia	Temp, °F	*H*, Btu/lbm (from measurements)	*H*, Btu/lbm (smoothed)
100	374.3	214.9	216.9
	385.5	247.4	247.4
	388.4	306.7	306.7
	389.9	361.3	361.3
	426.4	396.7	394.5
	451.0	408.2	409.5
	501.6	440.5	440.5
	551.8	472.8	471.5
	601.6	502.5	502.5

Storvick and Smith (*9–11*). The comparison in the vapor phase encompassed the temperature range 500–600°F and the pressure range 100–450 psia for the three mixtures studied.

The generalized method of Lydersen et al. (*2*) and Yen and Alexander (*15*) is formulated as:

$$(H^\circ - H)/T_c = f\,(T_r, P_r, Z_c) \qquad (7)$$

where $(H^\circ - H)/T_c$ is the enthalpy departure from ideal gas state, Btu/(lb-mol) (°R) or cal/(g-mol) (K); T_c, critical temperature, °R or K; T_r, reduced temperature, dimensionless; P_r, reduced pressure, dimensionless; and Z_c, compressibility factor at the critical point, dimensionless.

Lydersen's method is only applicable to nonpolar compounds and mixtures of nonpolar components.

McCracken et al. (*3*) and Storvick and Smith (*9–11*) have proposed a correlating procedure that relates the nonideal (polar–nonpolar) mixture enthalpies to the pure component values.

Their proposed equation is:

$$\Delta H = x_1{}^2\Delta H_1 + 2\,x_1x_2\Delta H_{12} + x_2{}^2\Delta H_2 + \Delta H_{\text{assoc}} \qquad (8)$$

where ΔH is the difference between the actual and ideal gas enthalpies for the polar–nonpolar mixture; ΔH_1, the difference between the actual and ideal gas enthalpies for the associating compound's homomorph; ΔH_2, the difference between the actual and ideal gas enthalpies for the nonassociating component in the mixture; ΔH_{12}, the interaction parameter taken as $\sqrt{\Delta H_1 \Delta H_2}$; x_1 and x_2, the mole fractions of each component; and ΔH_{assoc}, the enthalpy deviation owing to association obtained as subsequently explained.

To calculate ΔH_{assoc}, the enthalpies of the associating gas should be available and used in the following expressions:

$$\Delta H_t = \Delta H_s + \Delta H_g + \Delta H_{\text{assoc}} \qquad (9)$$

Table IV. Critical Constants of *n*-Pentanol–*n*-Heptane System

	Kay's rules		True critical constants	
n-Pentanol, %	T_c, °F	P_c, psia	T_c, °F	P_c, psia
25	533.2	432.6	510	400
50	553.9	468.4	544	490
75	574.5	504.2	570	535

Table V. Comparison of Entropies of Formation for Dimers and Trimers of Methanol, Ethanol, *n*-Propanol, and *n*-Pentanol

	ΔS_{f2}, Btu/(lb-mol) (°F)	ΔS_{f3}, Btu/(lb-mol) (°F)
Methanol (*9–11*)	−16.11	−42.99
Ethanol (*9–11*)	−16.04	−42.99
n-Propanol (*9–11*)	−17.13	−45.48
n-Pentanol, this work	−22.05	−56.76

Table VI. Differences Between Predicted and Experimental Enthalpies (Btu/lbm) of 25 Mol % *n*-Pentanol and 75 Mol % *n*-Heptane Mixture

Temp, °F	Press, psia	Lydersen (Kay's rules)	Lydersen (true critical constants)	Storvick
500	100	−0.69	−0.82	−0.12
	150	−3	−3.22	−1.52
	250	−9.92	−10.38	−3.52
550	100	−0.54	−0.61	−0.04
	150	−1.42	−1.52	−0.44
	250	−5.19	−5.32	−2.14
	350	−10.93	−10.59	−3.94
Average error, Btu/lbm		4.53	4.64	1.67
Percent error[a]		29.3	30.0	10.8

[a] Percent error calculated by dividing the sum of absolute errors by the sum of the experimental deviations from an ideal gas.

Table VII. Differences Between Predicted and Experimental Enthalpies (Btu/lbm) of 50 Mol % *n*-Pentanol and 50 Mol % *n*-Heptane Mixture

Temp, °F	Press, psia	Lydersen (Kay's rules)	Lydersen (true critical constants)	Storvick
500	100	−2.31	−2.86	−1.64
	150	−4.68	−5.5	−2.9
	250	−10.06	−11.63	−3.06
550	100	−1.42	−1.87	−1.33
	150	−2.4	−3.07	−2.03
	250	−7.27	−8.4	−5.13
	350	−12.9	−14.69	−7.51
600	100	−1.02	−1.37	−1.18
	150	−1.45	−1.97	−1.46
	250	−2.73	−3.56	−1.98
	350	−5.03	−6.22	−2.86
	450	−5.97	−8.9	−3.89
Average error, Btu/lbm		4.77	5.84	2.91
Percent error		28.3	34.6	17.3

Table VIII. Differences Between Predicted and Experimental Enthalpies (Btu/lbm) of 75 Mol % *n*-Pentanol and 25 Mol % *n*-Heptane Mixture

Temp, °F	Press, psia	Lydersen (Kay's rules)	Lydersen (true critical constants)	Storvick
500	100	−2.48	−3	−0.68
	150	−4.55	−5.34	−0.12
	250	−11.12	−12.68	2.79
550	100	−2.75	−3.18	−2.85
	150	−3.91	−4.55	−3.71
	250	−8.2	−9.29	−5.93
	350	−15.0	−16.74	−9.47
600	100	−1.78	−2.15	−2.27
	150	−3.03	−3.57	−3.62
	250	−6.48	−7.37	−6.45
	350	−10.08	−11.4	−8.75
	450	−15.2	−17.55	−12.82
Average error, Btu/lbm		7.05	8.07	4.96
Percent error		36.2	41.4	25.4

$$\Delta H_{\text{assoc}} = \sum_{n=2}^{\infty} - x_1{}^n P^{n-1} \Delta H_{fn} \exp\left[\frac{\Delta S_{fn}}{R} - \frac{\Delta H_{fn}}{RT}\right] \qquad (10)$$

where ΔH_t is the difference between the enthalpy of an associating gas at pressure P and the enthalpy of the gas in the ideal gas state; $\Delta H_s + \Delta H_g$, the geometric contribution to the difference ΔH_t (ΔH_s is the contribution for a compound which has spherical molecules and centrally located intermolecular force centers, and ΔH_g the additional contribution for nonspherical molecules with noncentral force centers. This sum is obtained directly from a generalized correlation applied to the homomorph of the associating compound); ΔH_{assoc}, the enthalpy difference due to association; x_1, the mole fraction of the associating compound remaining in monomeric form; P, total pressure; ΔH_{fn}, the heat of formation of the nth polymer; ΔS_{fn}, the entropy of formation of the nth polymer; and T, absolute temperature. The generalized correlation of Pitzer and coworkers (*4, 5*) may be used to obtain the enthalpies of the homomorphs.

In the application of the Storvick method in this work, the enthalpy data of *n*-pentanol (*12*) were satisfactorily represented by Equations 9 and 10, assuming only dimers and trimers were formed or that $n = 3$. The values obtained for the heats and entropies of formation for *n*-pentanol dimers and trimers are shown in Table V and compare favorably with those of other alcohols (methanol, ethanol, and *n*-propanol) reported in the literature (*3, 9–11*). Tables VI–VIII present the comparison of differences between predicted and experimental enthalpy deviations from the ideal gas values for the three mixtures (0.250, 0.500, 0.750 mole fraction *n*-pentanol).

The results showed that the method of Storvick and Smith is consistently superior to the method of Lydersen, either with Kay pseudocritical constants or with true critical values.

For the Lydersen method, the use of the true critical temperatures and pressures of the mixtures did not improve the enthalpy predictions; in fact, Kay's pseudocritical method (*7*) showed, for all the three mixtures studied, a slightly better prediction.

The method of Storvick and Smith was revealed to be good, particularly at low concentrations of *n*-pentanol.

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Supplementary Material Available. Extensive tabulation of the enthalpy data and large-scale enthalpy charts will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JCED-75-61.