Heats of Mixing of *n*-Alcohol-*n*-Alkane Systems at 15° and 55°C

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Heats of mixing of 17 binary *n*-alcohol-*n*-alkane systems were measured at 15° and 55°C in an isothermal dilution calorimeter.

An extensive body of accurate heat-of-mixing data is essential for the testing of models for predicting solution properties. Heats of mixing for *n*-alcohol-*n*-alkane systems have recently become increasingly available in the literature (*2, 8, 9*). However, the limited temperature range of these data was insufficient for our purposes in developing and testing the representation of mixtures by group solution models. An accurate semicontinuous isothermal calorimeter was therefore built and has been used to measure heats-of-mixing for *n*-alcohol-*n*-alkane systems at 15° and 55°C.

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Table I. Materials Employed

Material	Supplier & specification	Refractive index at 25°C	
		Exptl	Lit (*1*)
n-Hexane	Phillips Petroleum Co. Pure grade, 99+ mol %	1.3725	1.37226
n-Heptane		1.3850	1.38511
n-Octane		1.3954	1.39505
n-Nonane		1.4034	1.40311
n-Decane		1.4096	1.40967
n-Dodecane		1.4196	1.41949
Benzene		1.4979	1.4976
Cyclohexane		1.4235	1.4232
n-Butanol	Aldrich Chemical Co. 99 mol %	1.3970	1.3973
n-Pentanol		1.4079	1.4081
n-Hexanol		1.4160	1.4161
n-Octanol		1.4276	1.4275

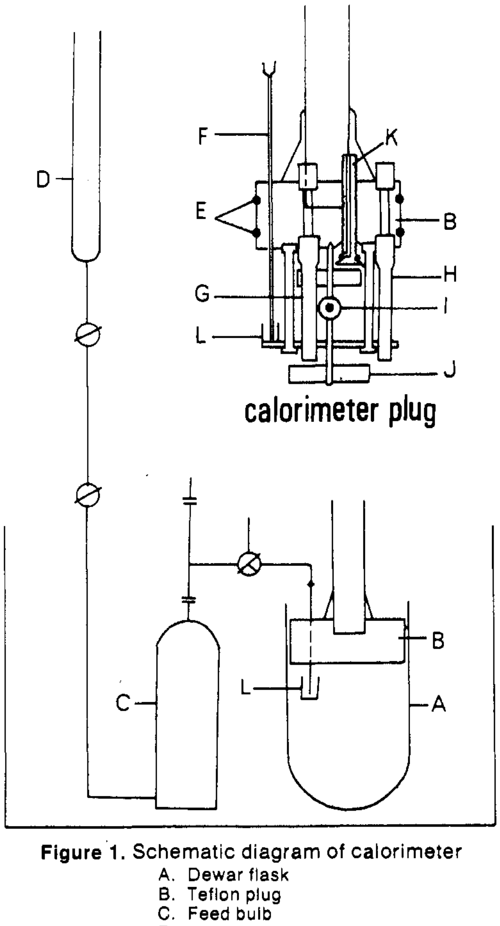

Figure 1. Schematic diagram of calorimeter
A. Dewar flask
B. Teflon plug
C. Feed bulb
D. Automatic buret
E. Viton "O" rings
F. Feed tube
G. Thermistor housing
H. Heater housing
I. Magnetic stirrer
J. Stirrer paddle
K. Vent screw
L. Teflon feed cup

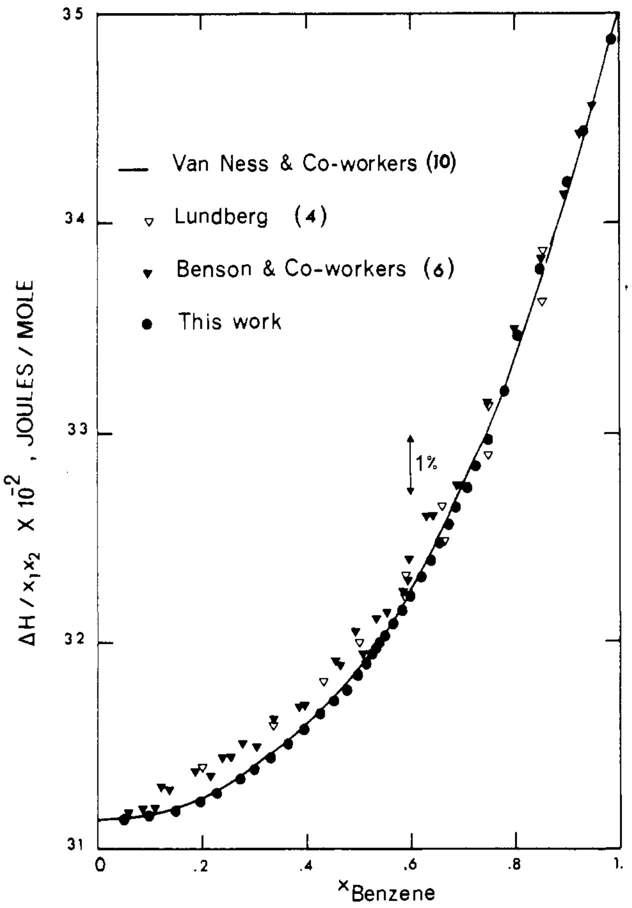

Figure 2. Heats of mixing at 25°C for system benzene-cyclohexane

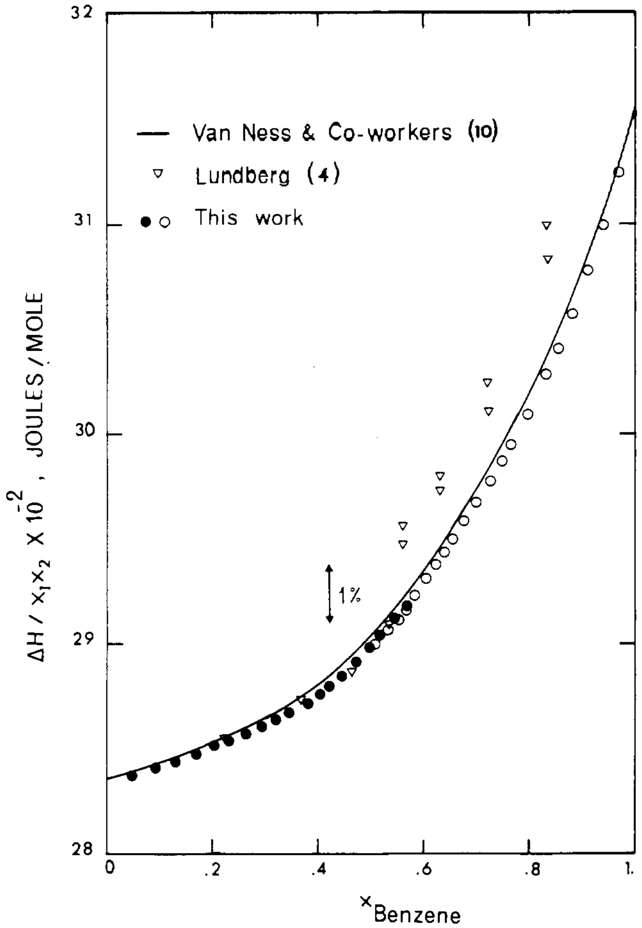

Figure 3. Heats of mixing at 50°C for system benzene–cyclohexane

Apparatus

The calorimeter was a slightly modified form of that developed by Van Ness and coworkers (*5, 10, 11*). Only a very brief description will be given here; further details are available elsewhere (*7*).

Figure 1 shows a schematic diagram of the calorimeter. One component to be mixed is weighed into the 250-ml Dewer flask (A), which is then sealed by the Teflon plug (B), all air being vented through the vent screw (K). The second component is stored in the feed bulb (C), which is connected through Teflon tubing to a water-jacketed, automatic buret (D). This arrangement (*8*) allows simple and fast operation with high precision.

Specifications of Materials

The specifications of the materials used in this work are given in Table I. Refractive indices were measured by a Baush & Lomb refractometer and agreed with literature values. The materials were used without further purification.

Experimental Results

To check the performance of the calorimeter, the heats of mixing of benzene and cyclohexane were measured at 25° and 50°C. The results are compared with those of other workers (*4, 6, 10*) in Figures 2 and 3. The values obtained with our calorimeter are internally consistent and in excellent agreement with the results of Van

Table II. Systems Studied

System	Temp, °C
n-Butanol–*n*-hexane	15
n-Butanol–*n*-heptane	15, 55
n-Butanol–*n*-octane	15, 55
n-Butanol–*n*-nonane	55
n-Butanol–*n*-decane	15
n-Butanol–*n*-dodecane	55
n-Pentanol–*n*-heptane	15
n-Pentanol–*n*-octane	55
n-Pentanol–*n*-nonane	55
n-Pentanol–*n*-decane	15
n-Pentanol–*n*-dodecane	55
n-Hexanol–*n*-heptane	15
n-Hexanol–*n*-octane	15, 55
n-Octanol–*n*-hexane	15
n-Octanol–*n*-heptane	15, 55
n-Octanol–*n*-octane	15, 55
n-Octanol–*n*-nonane	55
n-Octanol–*n*-decane	15
n-Octanol–*n*-dodecane	55

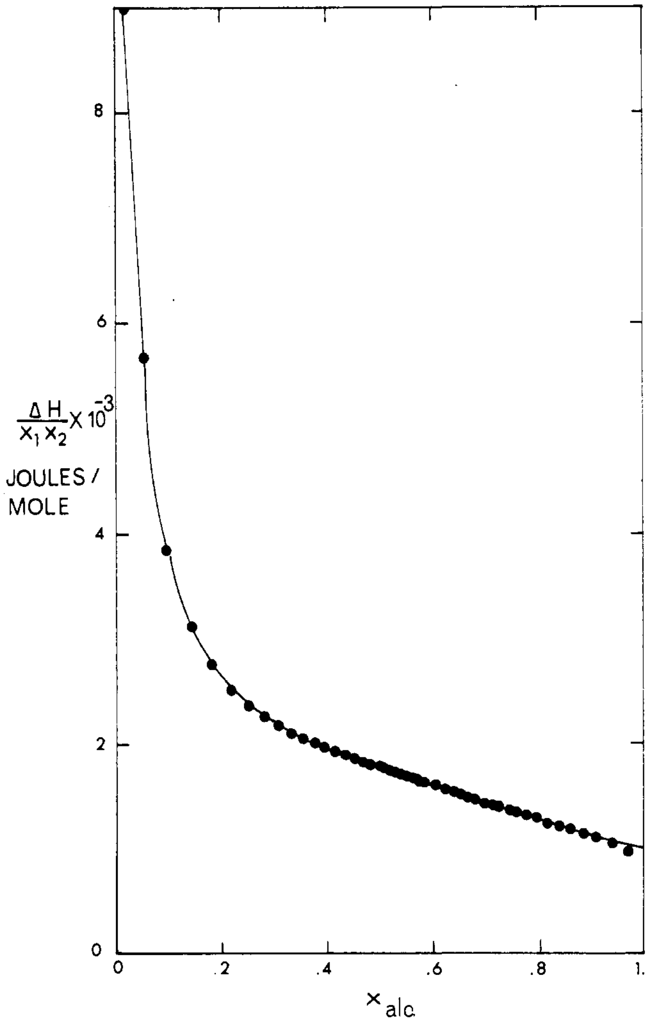

Figure 4. Heats of mixing at 15°C for system *n*-hexanol–*n*-octane

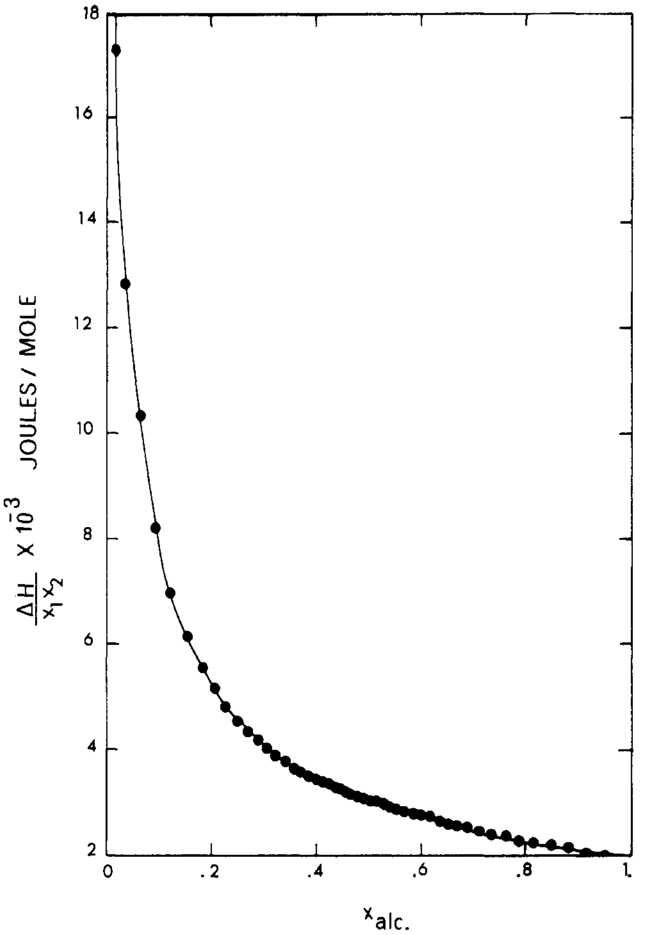

Figure 5. Heats of mixing at 55°C for system *n*-octanol–*n*-heptane

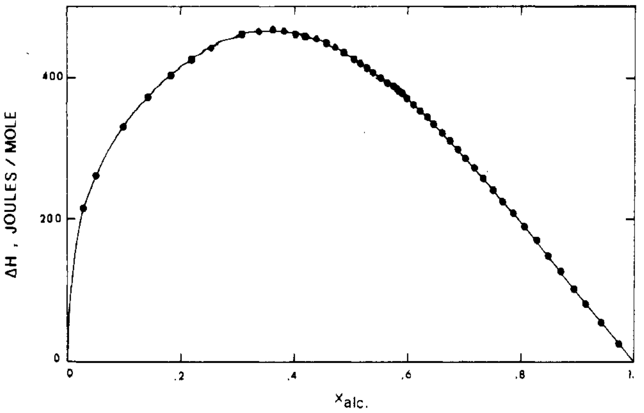

Figure 6. Heats of mixing at 15°C for system *n*-pentanol–*n*-heptane

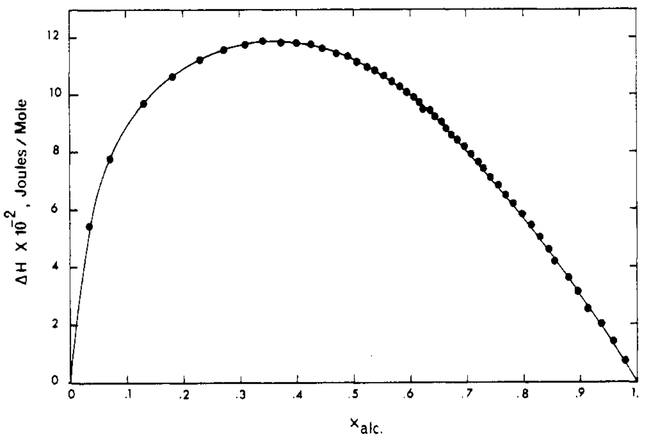

Figure 7. Heats of mixing at 55°C for system *n*-butanol–*n*-octane at 55°C

Table III. Heats of Mixing at 15°C for Binary *n*-Alcohol–*n*-Alkane Systems, J/Mol

$\frac{\Delta H}{x_1 x_2}$

x_{alc}	$C_4OH–C_6$	$C_4OH–C_7$	$C_4OH–C_8$	$C_4OH–C_{10}$	$C_5OH–C_7$	$C_5OH–C_{10}$
0.05	5270.5	5150.9	6191.6	6004.3	5425.9	6481.0
0.15	2947.0	2993.5	3397.6	3582.2	2928.9	3576.1
0.25	2318.8	2406.2	2687.6	2923.7	2383.2	2829.6
0.35	1979.2	2111.4	2353.4	2617.8	2020.2	2536.8
0.45	1727.6	1884.3	2116.1	2411.1	1830.0	2345.4
0.55	1521.7	1704.4	1934.7	2269.5	1620.2	2201.2
0.65	1358.7	1550.7	1796.4	2173.2	1456.2	2039.5
0.75	1231.4	1417.3	1683.5	2133.1	1290.7	1932.6
0.85	1141.5	1313.4	1601.1	2101.0	1153.4	1836.5
0.95	1178.6	1199.3	1560.2	2111.8	987.5	1746.1

x_{alc}	$C_6OH–C_7$	$C_6OH–C_8$	$C_8OH–C_6$	$C_8OH–C_7$	$C_8OH–C_8$	$C_8OH–C_{10}$
0.05	5365.9	5704.3	4693.7	5138.6	5446.7	6022.3
0.15	2826.0	3040.3	2400.2	2646.1	2814.7	3145.0
0.25	2200.5	2372.6	1816.0	2009.8	2143.9	2411.5
0.35	1900.2	2056.6	1550.5	1721.3	1838.8	2079.5
0.45	1705.7	1869.6	1355.2	1544.0	1655.9	1900.4
0.55	1516.9	1697.7	1192.8	1413.8	1505.9	1783.6
0.65	1342.6	1529.7	1062.7	1279.1	1365.2	1668.2
0.75	1195.4	1368.9	924.7	1116.7	1215.6	1536.0
0.85	1014.4	1209.4	794.6	917.3	1070.5	1410.8
0.95	829.6	1027.9	616.1	758.0	909.4	1185.2

Table IV. Heats of Mixing at 55°C for Binary *n*-Alcohol–*n*-Alkane Systems, J/Mol

$$\frac{\Delta H}{x_1x_2}$$

x_{alc}	$C_4OH–C_7$	$C_4OH–C_8$	$C_4OH–C_9$	$C_4OH–C_{12}$	$C_5OH–C_8$	$C_5OH–C_9$
0.05	13541.6	14119.3	14671.4	16136.7	13630.9	14196.2
0.15	7509.2	7955.6	8369.7	9445.0	7566.3	7990.4
0.25	5726.2	6086.0	6439.7	7356.7	5739.5	6062.7
0.35	4867.0	5208.1	5518.1	6330.6	4863.7	5255.2
0.45	4330.2	4672.5	4977.1	5760.9	4351.2	4869.4
0.55	3955.8	4318.8	4619.8	5417.1	3993.8	4445.4
0.65	3618.0	3997.6	4364.2	5214.8	3691.6	4096.7
0.75	3359.8	3733.4	4163.5	5100.7	3443.9	3860.7
0.85	3145.0	3539.9	3992.9	5074.2	3227.3	3670.2
0.95	2956.5	3363.1	3846.5	5143.1	3015.6	3446.6
x_{alc}	$C_5OH–C_{12}$	$C_6OH–C_8$	$C_8OH–C_7$	$C_8OH–C_8$	$C_8OH–C_9$	$C_8OH–C_{12}$
0.05	15493.5	13177.5	11001.3	12518.7	12469.6	14711.5
0.15	9131.6	7199.2	6179.5	6695.4	6942.1	8302.6
0.25	7017.6	5396.5	4557.5	4893.8	5149.7	6206.4
0.35	6021.3	4527.7	3748.4	4033.3	4296.1	5162.8
0.45	5455.0	4012.0	3242.2	3528.2	3820.1	4563.9
0.55	5144.5	3653.0	2888.2	3178.6	3503.1	4190.5
0.65	4926.9	3358.9	2617.6	2914.6	3213.1	3930.1
0.75	4779.7	3127.2	2400.6	2702.9	3005.6	3750.5
0.85	4706.2	2913.6	2201.0	2509.8	2811.0	3599.7
0.95	4645.6	2698.1	1996.6	2338.6	2626.4	3459.2

Ness and coworkers (*10*). Their data are represented by the solid curves, which have a root-mean-square deviation of about 0.1% from their experimental points.

Whether the small discrepancies between the data are due to reagent impurities or to systematic errors in the calorimeters, it seems likely that the values obtained with the present calorimeter are within 1% of the true heats of mixing of benzene and cyclohexane at 25° and 50°C. For other systems with comparable heats of mixing such as alcohol–hydrocarbon systems, it seems reasonable to assume a similar accuracy.

Table II shows the binary *n*-alcohol-*n*-alkane systems studied at 15° and 55°C. The experimental data all lie on smooth curves, as can be seen from the typical results shown in Figures 4–7. The original data were judged to be too extensive to reproduce here, and all 24 sets have consequently been filed with the National Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Ont., Canada.

The expanded spline-fit technique (*3*) was used to represent the experimental values of $\Delta H/x_1x_2$. Interpolated values of $\Delta H/x_1x_2$ from the spline-fits are presented in Tables III and IV for data at 15° and 55°C, respectively.

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Nomenclature

x = mole fraction

ΔH = heat of mixing per mole of mixture

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