benzene, toluene, and xylenes.

Literature Cited

(1) Adcock, D. S., McGlashan, M. L., *Proc. R. Soc. London*, **57**, 581 (1961).
(2) Andrew, A. W., Morcom, K. W., *J. Chem. Thermodyn.*, **3**, 519 (1971).
(3) Beath, L. A., Neill, S. P. O., Williamson, A. G., *J. Chem. Thermodyn.*, **1**, 293 (1969).
(4) Brown, I., Smith, F., *Aust. J. Chem.*, **15**, 1 (1962).
(5) Cabani, S., Ceccanti, N., *J. Chem. Thermodyn.*, **5**, 9 (1973).
(6) Dincer, S., VanNess, H. C., *J. Chem. Eng. Data*, **16**, 378 (1971).
(7) Geier, K., Bittrich, H. J., *Z. Phys. Chem.* (*Leipzig*), **255**, 305 (1974).
(8) Guillen, M. D., Otin, S., Gracia, M., Gutierrez Losa, C. G., *J. Chim. Phys. Phys.-Chim. Biol.*, **72**, 425 (1975).
(9) Kehiaian, H. V., *J. Chim. Phys. Phys.-Chim. Biol.*, **68**, 935 (1971).
(10) Mahl, B. S., Khurma, J. R., *J. Chem. Soc., Faraday Trans. 1*, **73**, 29 (1977).
(11) Mahl, B. S., Kooner, Z. S., Khurma, J. R., *J. Chem. Thermodyn.*, **9**, 61 (1977).
(12) Mahl, B. S., Nigam, R. K., Chopra, S. L., Singh, P. P., *J. Chem. Thermodyn.*, **3**, 363 (1971).
(13) Meyer, R., Giusti, G., Meyer, M., Vincent, E. J., *Thermochim. Acta*, **13**, 379 (1975).
(14) Meyer, R., Meyer, M., Bares, D., Vincent, E. J., *Thermochim. Acta*, **11**, 211 (1975).
(15) Murakami, S., Koyama, M., Fujishiro, R., *Bull. Chem. Soc. Jpn.*, **41**, 1540 (1968).
(16) Nigam, R. K., Mahl, B. S., *J. Chem. Soc., Faraday Trans. 1*, **68**, 1508 (1972).
(17) Nigam, R. K., Singh, P. P., *Trans. Faraday, Soc.*, **65**, 950 (1969).
(18) Quitzsch, K., *J. Prakt. Chem.*, **35**, 49 (1967).

Received for review June 3, 1977. Accepted November 8, 1977.

Experimental Heats of Mixing of Some Miscible and Partially Miscible Nonelectrolyte Systems

G. L. Nicolaides and C. A. Eckert*

Department of Chemical Engineering, University of Illinois, Urbana, Illinois 61801

The isothermal dilution calorimeter has been modified by some improvements in the electronics of temperature control and heat addition, to facilitate the ease of measurements. Endothermic heats of mixing are shown to be in good agreement with existing data for two test systems; new results are reported for eight additional binary mixtures: hexane–nitrobenzene at 25 and 50 °C; hexane–nitroethane at 35 and 50 °C; cyclohexane–aniline at 35 and 50 °C; acetone–ethanol at 25 and 50 °C; chlorobenzene–1-nitropropane at 25 and 50 °C; ethanol–chlorobenzene at 25 and 50 °C; cyclohexane–furfural at 75 °C; and methylcyclohexane–furfural at 75 °C.

Although traditional methods of solution thermodynamics have primarily been centered on the determination of activity coefficients through phase equilibrium measurements, the prediction and correlation of the heat of mixing are now being recognized as an important step toward a generally valid representation of liquid mixture nonidealities. As a direct measure of the temperature dependence of the excess Gibbs energy, the heat of mixing can be used to evaluate semitheoretical Gibbs energy expressions; it can also be viewed as a potential alternative to classical vapor–liquid equilibria measurements. Until the development of the Van Ness-type isothermal dilution calorimeter (*11*, *15*), reliable heat of mixing measurements were often considered exceptionally difficult and were attempted only infrequently. On the other hand, no theoretical expression suggested the possibility of simultaneously representing or cross-predicting heats of mixing and vapor–liquid equilibria until the appearance of the Wilson equation (*13*) and other local composition models that followed (*1*, *5*, *10*).

As part of our effort to establish a data base for the evaluation of different liquid models, an isothermal dilution calorimeter of the Van Ness (*11*, *15*) type was developed and data were obtained for three miscible and five partially miscible nonelectrolyte systems. These results have been combined elsewhere (*8*, *9*) with phase equilibria and additional heats of mixing from the literature and used to investigate the utility of local composition equations in representing, extrapolating, and cross-predicting the different types of binary data. The combination of heats of mixing and activity coefficients at infinite dilution, the latter measured directly with a newly developed technique (*3*), has been found sufficient to describe completely the nonideality of miscible systems over a reasonable temperature range.

Apparatus

The calorimeter is shown schematically in Figures 1 and 2. The mixing occurs in a Dewar flask sealed by a moving Teflon piston. One component is weighed into the flask and then all vapor is eliminated through a vent as the piston is lowered. With the vent closed, the piston is raised to draw in the second component, which flows into the vessel through a stainless steel capillary tube and a mercury seal, under the pressure of a mercury column. Heat is added quantitatively at the same time to compensate for the endothermic mixing so that the system is kept isothermal. The composition of the mixture after each addition of the second component is determined by weighing into the solute reservoir a volume of mercury equal to that of the liquid added to the mixture.

Several advantages accrue from this type of calorimeter. The complete absence of a vapor space eliminates the necessity for any heat of vaporization correction, a substantial source of uncertainty in older calorimeter designs. In addition, the semicontinuous introduction of the solute, compared to various diaphragm-rupturing arrangements, permits the determination of as many data points as needed during a run and of all the data for a binary system in two runs. The measurement of the heat of mixing at very dilute concentrations is also facilitated. Finally, the isothermal operation of the instrument minimizes heat losses or gains through the calorimeter piston and, above all, obviates any absolute measurements other than those of the heat added quantitatively and the gravimetric determinations of composition.

The calorimeter was designed to combine simplicity of construction and operation and accuracy of better than 1%. The Dewar mixing vessel is 8 in. high and has a 2-in. inner diameter of precision bore tubing. It is held stationary relative to the solute reservoir which is about 4 in. high and 2 in. in diameter with a 16 in. high, 0.3 in. diameter column at its center where mercury is contained. The column broadens into a

0021-9568/78/1723-0152$01.00/0

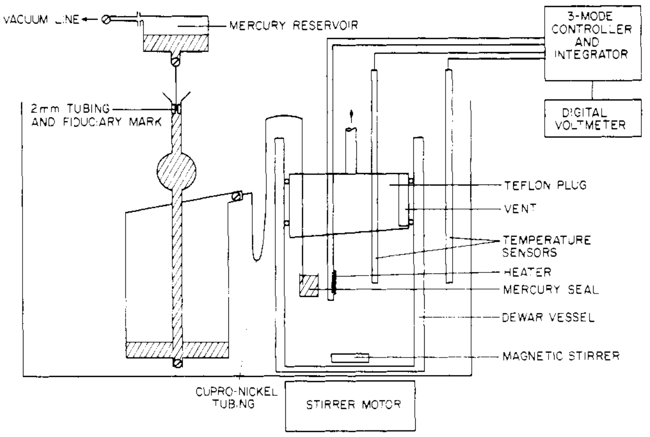

Figure 1. Schematic of isothermal dilution calorimeter.

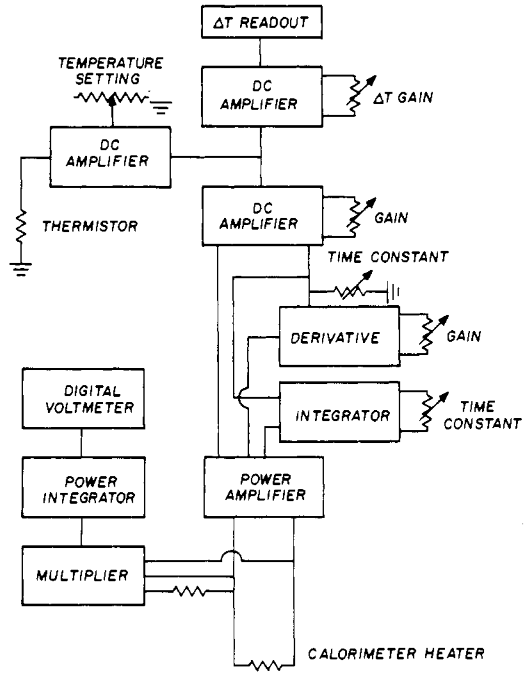

Figure 2. Calorimeter circuit block diagram.

10-cm^3 bulb right above the top of the main vessel and ends as a small funnel above a 0.25-in. piece of 2-mm precision bore tubing. A fiduciary mark on this tubing aids the maintenance of the mercury level in the column. Mercury is added from, or withdrawn into, a 50-cm^3 reservoir to which a needle and a vacuum line are attached as shown in Figure 1. The reservoir is positioned so that the tip of the needle is at the level of the fiduciary mark. The two main vessels are connected by flexible $^3/_{64}$-in. cupronickel tubing. On the solute reservoir side, the tubing is soldered to a 14-gauge steel hypodermic needle epoxied to a luer joint at the end of a 2-mm Teflon stopcock, while on the mixing vessel side it is connected to a steel tube passing through the Teflon piston. The piston is moved in and out of the Dewar by means of a rider mounted on a threaded brass rod turned manually, and the whole assembly can be lowered into a constant-temperature water bath which is controlled by a Hallikainen (Thermotrol 1053B) controller. Stirring in the mixing vessel is accomplished with a 0.75-in. Teflon-coated magnetic bar activated by a stirrer motor located directly under the water bath. The bath consists of an insulated 12-in. battery jar kept at temperatures constant to 0.001 °C.

The Teflon piston is 1.98 in. in diameter and 1.25–1.5 in. thick, slightly slanted at the bottom to facilitate the venting of all vapor. Dual O-rings, of solvent-resistant materials, give the actual seal. Right under the lower O-ring and at the point of minimum plug thickness, a horizontal vent hole was drilled, connecting the very top of the mixing space to a vertical opening, sealed at the top by a needle valve.

Also passing through the Teflon piston are the solute feed tube, a thermometer probe, two heater leads, and a cooling coil. All these were forced through the Teflon after undersize holes were drilled, thus forming tight seals directly. The feed tube is an 18-gauge steel needle extending 1.5 in. into the vessel with its tip at the bottom of a 0.5-cm^3 Teflon cup attached to the lower end. This cup is filled with mercury that forms a seal to

Table I. Heats of Mixing of Benzene (1)-Cyclohexane (2) at 25 °C

x_1	h^E, J/mol This work	 Stokes[a]	 Van Ness[a]	% deviation from Stokes	 Van Ness
0.0914	283.89	285.04	284.27	−0.40	−0.13
0.0947	295.64	293.90	293.11	0.59	0.86
0.1769	488.79	489.60	488.55	−0.17	0.05
0.1850	509.85	505.95	504.88	0.77	0.98
0.2737	655.40	655.69	654.43	−0.04	0.15
0.2786	668.60	662.27	660.99	0.96	1.15
0.3694	757.26	756.60	755.05	0.09	0.29
0.3768	768.85	761.94	760.37	0.91	1.11
0.4710	804.86	799.05	797.14	0.73	0.97
0.4748	801.21	799.38	797.46	0.23	0.47
0.5301	798.06	794.12	792.02	0.50	0.76
0.5616	781.87	782.77	780.60	−0.11	0.16
0.5958	767.27	763.59	761.36	0.48	0.77
0.6303	736.08	737.03	734.79	−0.13	0.17
0.6507	720.71	718.00	715.78	0.38	0.69
0.7059	652.39	653.79	651.69	−0.21	0.11
0.7201	636.17	634.30	632.26	0.29	0.62
0.7866	526.03	526.77	525.08	−0.14	0.18
0.8003	501.53	501.32	499.73	0.04	0.36
0.8992	283.70	283.43	282.66	0.09	0.37
0.9273	210.71	210.74	210.22	−0.02	0.23

[a] Smoothed data from eq 1.

Table II. Heats of Mixing of Carbon Tetrachloride (1)-Benzene (2) at 25 °C

x_1	h^E, J/mol This work	 Stokes[a]	 Van Ness[a]	% deviation from Stokes	 Van Ness
0.1033	46.81	46.21	45.62	1.30	2.58
0.2020	78.65	78.14	77.06	0.65	2.03
0.3042	100.74	100.30	98.92	0.44	1.82
0.4076	112.67	112.59	111.15	0.07	1.35
0.4721	114.36	115.43	114.07	−0.92	0.25
0.4963	115.35	115.56	114.25	−0.18	0.95
0.5701	111.76	112.88	111.74	−0.99	0.02
0.6854	98.17	99.29	98.50	−1.13	−0.33
0.8002	72.92	74.05	73.58	−1.53	−0.89
0.8916	44.38	45.13	44.87	−1.66	−1.09

[a] Smoothed data from eq 1.

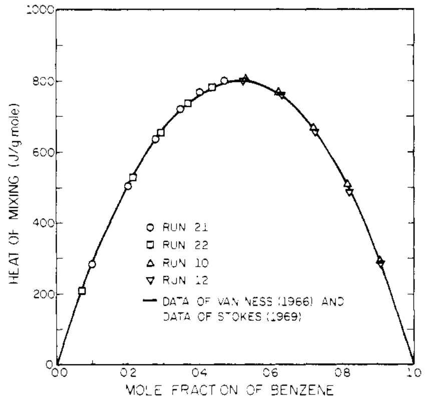

Figure 3. Heat of mixing for the benzene–cyclohexane system at 25 °C.

Table III. Measured Heats of Mixing

Hexane (1)-Nitrobenzene (2) (T_c = 20 °C)

25 °C				50 °C			
x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol
0.0579	316.51	0.5164	1436.00	0.0413	212.95	0.4954	1492.93
0.1177	605.40	0.5804	1444.50	0.0909	454.51	0.5955	1481.80
0.2173	991.97	0.6870	1355.60	0.1983	912.21	0.6892	1384.29
0.3164	1254.78	0.7684	1207.29	0.3286	1288.27	0.7856	1173.75
0.4165	1398.65	0.8723	859.71	0.4043	1420.74	0.8954	731.30
0.4927	1451.32	0.9314	543.08	0.4889	1500.36	0.9445	436.90

Results of Fit to Equation 1

A = 5684.42
B = 2391.77
C = −10 216.01
D = 11 673.04
Std % dev = 0.437

A = 5207.12
B = 4321.40
C = −10 495.09
D = 9971.14
Std % dev = 0.272

Hexane (1)-Nitroethane (2) (T_c = 31 °C)

35 °C				50 °C			
x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol
0.0770	597.40	0.5005	1733.20	0.0458	372.03	0.3938	1762.29
0.1258	894.80	0.5583	1723.30	0.0955	716.82	0.4860	1827.33
0.2326	1352.80	0.6914	1600.50	0.1724	1140.01	0.5843	1806.48
0.3252	1564.00	0.8089	1305.00	0.2215	1347.53	0.6797	1691.55
0.3552	1645.70	0.8821	975.00	0.2930	1567.67	0.7784	1442.25
0.4019	1692.40	0.9381	606.00	0.3394	1673.05	0.8791	992.83
0.4234	1677.80			0.3559	1710.39	0.9424	557.34

Results of Fit to Equation 1

A = 8794.04
B = −5084.38
C = −2735.67
D = 10 591.60
Std % dev = 0.867

A = 8671.38
B = −3773.30
C = −2071.51
D = 8296.26
Std % dev = 0.338

Cyclohexane (1)-Aniline (2) (T_c = 30 °C)

35 °C				50 °C			
x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol
0.0483	427.18	0.4806	1869.78	0.0477	423.10	0.4505	2017.36
0.0994	804.99	0.5758	1853.76	0.0911	748.71	0.5421	2062.57
0.1751	1235.59	0.6784	1765.73	0.1675	1219.50	0.6456	1998.68
0.2771	1613.24	0.7827	1564.99	0.2626	1631.80	0.7664	1752.60
0.3691	1798.80	0.8795	1178.97	0.3599	1887.64	0.8718	1289.81
0.4683	1883.49	0.9444	692.58	0.4438	2025.86	0.9296	847.01

Results of Fit to Equation 2

A = 9717.02
B = −8982.84
C = 16 759.87
D = −28 242.65
E = 26 100.37
Std % dev = 0.424

A = 9640.97
B = −7630.41
C = 15 784.39
D = −22 187.28
E = 19 505.97
Std % dev = 0.321

Acetone (1)-Ethanol (2) (Miscible)

25 °C				50 °C			
x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol
0.0418	180.67	0.4729	1108.17	0.0481	237.71	0.4045	1196.43
0.0853	357.17	0.5430	1110.11	0.1032	477.09	0.5170	1235.91
0.1607	611.18	0.6456	1040.48	0.1983	799.28	0.6099	1184.48
0.2704	879.66	0.7619	850.41	0.2991	1038.71	0.7109	1037.55
0.3561	1015.55	0.8600	583.07	0.3825	1166.15	0.8040	806.10
0.4507	1098.30	0.9317	316.39	0.4654	1226.43	0.9068	439.92
						0.9510	244.76

Results of Fit to Equation 2

A = 4517.08
B = 670.30
C = −5256.23
D = 9360.79
E = −4222.11
Std % dev = 0.417

A = 5272.53
B = −1545.62
C = 1717.76
D = 387.69
E = −537.89
Std % dev = 0.286

Chlorobenzene (1)-1-Nitropropane (2) (Miscible)

25 °C				50 °C			
x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol
0.0561	17.07	0.4823	107.18	0.0453	19.05	0.4916	140.43
0.1084	31.94	0.5472	112.74	0.0950	36.30	0.5878	161.25
0.2005	55.93	0.6660	115.09	0.1850	66.76	0.7055	157.51
0.2982	78.71	0.7709	104.44	0.2897	98.64	0.8064	138.94
0.3861	95.91	0.8853	70.98	0.3968	123.15	0.8974	99.75
		0.9324	48.05			0.9502	61.58

Results of Fit to Equation 2

A = 313.86
B = 116.17
C = 459.60
D = −745.53
E = 719.50
Std % dev = 0.616

A = 475.42
B = −943.81
C = 5175.89
D = −8158.65
E = 4946.95
Std % dev = 2.689

Table III (Continued)

Ethanol (1)-Chlorobenzene (2) (Miscible)

25 °C				50 °C			
x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol
0.0796	549.77	0.5219	552.26	0.0411	499.07	0.5583	915.56
0.1343	657.60	0.6502	398.97	0.0794	758.23	0.5824	899.98
0.2315	725.46	0.6978	330.31	0.1733	1047.56	0.6086	849.49
0.3200	715.30	0.7952	215.30	0.2793	1145.36	0.6928	674.49
0.4182	654.71	0.8859	79.99	0.3836	1118.45	0.7998	430.74
		0.9418	29.02	0.4819	1026.05	0.9041	189.91
						0.9440	104.23

Cyclohexane (1)-Furfural (2) (T_c = 65 °C)

75 °C

x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol
0.0534	417.89	0.2840	1713.45	0.5055	2130.87	0.8084	1602.91
0.1053	789.78	0.3639	1944.53	0.6084	2091.21	0.9050	1011.81
0.1903	1287.89	0.4353	2072.95	0.7075	1939.66	0.9544	533.60

Results of Fit to Equation 2

A = 8027.87
B = 5131.35
C = −20 962.43
D = 29 094.70
E = −8148.78
Std % dev = 0.766

Methylcyclohexane (1)-Furfural (2) (T_c = 70 °C)

75 °C

x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol
0.0391	339.09	0.1698	1277.06	0.3405	1981.84	0.7521	1778.99
0.0828	694.87	0.2621	1722.56	0.5261	2060.16	0.8634	1227.03
				0.6494	1983.76	0.9163	839.21

Results of Fit to Equation 2

A = 8699.02
B = 8928.04
C = −47 824.54
D = 72 653.10
E = −30 744.42
Std % dev = 1.251

keep the two components apart when the piston is stationary. The thermometer probe is a glass-coated bead thermistor (Fenwall, GA45P2) in a stainless steel tube $^3/_{16}$ in. in diameter, of 0.010 in. wall thickness, extending 1 in. under the plug. Some mineral oil was added to the tube to facilitate the conduction of heat to the thermistor. The heater leads are brass bars $^1/_{16}$ in. in diameter extending 1.25 in. into the vessel with the heater, a coil of chromel 36 gauge wire of about 30 Ω, soldered on. The cooling coil is of cupronickel tubing $^1/_{32}$ in. in diameter soldered to 18 gauge steel tubes passing through the piston.

The thermistor and heater leads are connected to a 3-mode high-precision temperature controller designed for this particular application. This instrument, with the accompanying integrator circuit described below, does not improve the precision of the data but substantially facilitates the ease of data acquisition. Not shown on the figure is a second temperature probe that can be switched in for monitoring the water bath temperature. A digital voltmeter (Model 190, Keithley Instruments) or a recorder (Sargent Welch, Model SRG) is used to read the temperature difference from a set point while the same difference is automatically fed to the circuit controlling the heater. The set point is always adjusted so that the output from the thermistor on the piston is zero at the temperature of the bath. The sensitivity of the output can be adjusted for each set temperature to 1 V/degree of deviation. Output noise levels are usually well below 0.0005 V so that the temperature can be monitored to 0.001 °C. The heater voltage and current are both measured and then multiplied while their product is integrated. The integrated power is read on the digital voltmeter at the end of every solute injection into the mixing vessel. Details of the temperature-monitoring circuit and of the heat-measurement circuit are given elsewhere (*9*).

Procedure

At the beginning of the run, solute is added to the reservoir where it is contained by the Teflon stopcock at the upper end and by mercury added to the central column. The cupronickel tubing is then connected and any air trapped is eliminated by bleeding the pressurized system through the mercury seal at the other side. The surface of the mercury in the Teflon cup is dried while the mercury level in the column is brought to just above the 10-cm^3 bulb. About 100 cm^3 of the solvent is weighed into the Dewar vessel and the plug is quickly lowered, with the vent open, until there is no vapor space left, whereupon the vent is closed. With the Teflon stopcock still closed, the system is lowered into the water bath. The water level is a few inches above both the Dewar vessel and the 10-cm^3 bulb on the mercury column. The solute reservoir is then allowed to come to thermal equilibrium with the bath. Mercury is allowed to flow into the central column and, after the fiduciary mark has been reached, the excess mercury is drawn back into its reservoir by the vacuum applied at the top. The latter process is repeated to maintain the mercury level constant as the fluid expands thermally. To connect the two main vessels after the solute reservoir has come to the bath temperature, the Teflon stopcock between them is opened while downward pressure is applied to the plug causing the mercury in the column to rise briefly before the plug is returned to its previous position. In this manner, no solute escapes into the mixing vessel as a result of lower pressure there before the stopcock is opened. With the two vessels connected, the stirrer and the heater are switched on so that the Dewar can be brought to the bath temperature by the controller. To accommodate the expansion of the solvent during the heating, the plug is periodically moved up so that the mercury level in the column remains at the fiduciary mark. After the solvent has been brought to thermal equilibrium with the bath, its temperature is recorded for 0.5 h with the heater off to make sure the plug and other parts are not still absorbing heat. The stirring rate is adjusted so that any visible effect it has on the calorimeter temperature is negligible—400–500 rpm. The cooling coil is used when the mixing vessel temperature rises above the bath temperature, during the preliminary heating, to bring the vessel below the set point; it is not used during an actual run. (Heat cannot be removed quantitatively with a cooling coil. For exothermic systems, the calorimeter would have to be operated adiabatically or be modified through the addition of a Peltier device. Winterhalter and Van Ness (*14*, *15*) have used such a device to measure exothermic heats of mixing.)

For runs made at higher temperatures (50 and 75 °C), a slightly different procedure is used, since heat leaking through the plug, before the Teflon stopcock is opened, causes an increase of the pressure in the system sufficient to rupture the cupronickel-to-steel joints. Instead of eliminating all vapor when the plug is lowered, a few milliliters are left in when the vent is closed, and then the plug is raised so that the pressure in the vessel is decreased. The vapor space is eliminated after thermal equilibrium is nearly established.

The introduction of the second component into the calorimeter vessel is begun by moving the plug up slowly. As soon as some of the solute has flowed in, the temperature in the vessel is seen to drop while the controller, mainly in its derivative mode, supplies heat to compensate at a rate of up to 3 W. By monitoring the temperature in the vessel continuously, the introduction of the second component can be regulated manually so that the temperature will oscillate about the set point with a maximum deviation in either direction of 0.010 °C during one solute injection. Thus, heat losses and gains through the plug or walls are kept small and approximately balanced. The latter assertion is verified by the output of the integral mode in the controller being nearly zero at the end of every injection. Usually, when enough solute has been introduced for a data point to be recorded, the heater is switched off while the temperature deviation is slightly positive and the system is brought to within 0.001 °C of the set point by carefully adding minute amounts of solute. The integrated power is then read and recorded, the mercury level restored to the fiduciary mark, and the mercury reservoir weighed. From the change in the reservoir weight before and after every injection, the densities of the solute and of mercury at the bath temperature, and the initial weight of solvent, the composition of the mixture can be calculated easily at every point while the recorded integrated power and the total number of moles in the mixture give the heat of mixing at that composition.

Preparing the instrument and completing one run of six data points takes 6–7 h so that data for one binary system at one temperature (two runs) could be obtained in 1 day. Further details of the equipment and procedure are available elsewhere (*9*), as are the details of solvent and solute purifications (*3*, *8*).

Tests on Standard Systems

To test the performance of the calorimeter, the heats of mixing of the benzene–cyclohexane and the benzene–carbon tetrachloride systems at 25 °C were measured. These are the systems most often used to test calorimeters (*2*, *4*, *6*, *7*, *11*, *12*), the latter forming a particularly severe test as the heat of mixing is relatively low and the densities of the two components quite different. The results were compared to those of Stokes (*12*) and of Van Ness (communicated to Stokes). Stokes has also compared his data to those of Larkin and McGlashan (*6*), Lundberg (*7*), and Bennett and Benson (*2*). Data from four runs with the benzene–cyclohexane system are presented in Table I and Figure 3. The results of Stokes and of Van Ness represent smoothed values calculated from the equation

$$h^E(\mathrm{J\ mol^{-1}}) = x_1x_2(A + Bx_1 + Cx_1^2 + Dx_1^3) \qquad (1)$$

where x_1 and x_2 are the mole fractions of the two components in the mixture. Values for the constants are given in ref 12. The data obtained in this work are generally within 1% of the calculated, smoothed values of the previous authors. Table II and Figure 3 show a similar comparison of data for the benzene–carbon tetrachloride system. Here the percent difference between any two authors is slightly higher owing to the lower heat of mixing values.

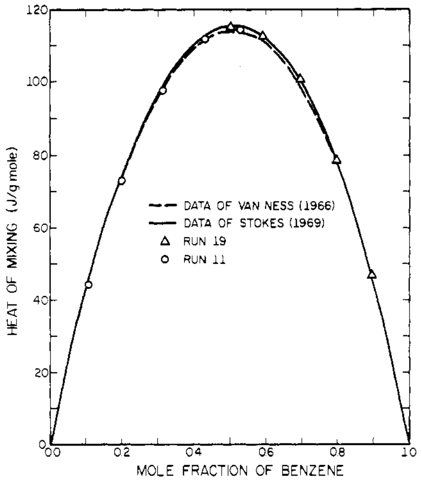

Figure 4. Heat of mixing for the benzene–carbon tetrachloride system at 25 °C.

Results

New results obtained for eight systems are given in Table III. The consolute temperatures T_c of the partially miscible mixtures are given; all heat of mixing data were taken at temperatures above these upper critical solution temperatures. The data were fit to eq 1 with a fifth, quartic term included whenever this improved the fit.

$$h^E(\mathrm{J\ mol^{-1}}) = x_1x_2(A + Bx_1 + Cx_1^2 + Dx_1^3 + Ex_1^4) \qquad (2)$$

The constants for eq 1 or 2 are included together with the standard percent deviations of the fit, usually better than 1%, as a measure of consistency. It should be noted that these fits are reported only for convenience; such a fit is not always an appropriate test for data since the form of this Margules-type equation may be quite unsuitable for the heat of mixing of many systems; it is omitted altogether for the ethanol–chlorobenzene system. A discussion of alternate analytical forms for excess enthalpy data is presented elsewhere (*8*, *9*).

Acknowledgment

The authors thank R. Anderson and C. J. Hawley, Jr., for aid in the design of the control and integration electronics.

Literature Cited

(1) Abrams, D. S., Prausnitz, J. M., *AIChE J.*, **21**, 116 (1975).
(2) Bennett, J. E., Benson, G. C., *Can. J. Chem.*, **43**, 1912 (1965).
(3) Eckert, C. A., Newman, B. A., Nicolaides, G. L., Long, T. C., *AIChE J.*, paper submitted.
(4) Elliott, K., Wormald, C. J., *J. Chem. Thermodyn.*, **8**, 881 (1976).
(5) Hsieh, C. K., Eckert, C. A., "The Zeta Equation-A New Solution to the Gibbs-Duhem Equation", presented at the 71st National AIChE Meeting, Tulsa, Okla., March 12, 1974.
(6) Larkin, J. A., McGlashan, M. L., *J. Chem. Soc.*, 3425 (1961).
(7) Lundberg, G. W., *J. Chem. Eng. Data*, **9**, 193 (1964).
(8) Nicolaides, G. L., Eckert, C. A., "Optimal Representation of Binary Liquid Mixture Nonidealities", submitted to *Ind. Eng. Chem. Fundam.*
(9) Nicolaides, G. L., Ph.D. Thesis, University of Illinois, Urbana, 1977.
(10) Renon, H., Prausnitz, J. M., *AIChE J.*, **14**, 135 (1968).
(11) Savini, C. G., Winterhalter, D. R., Kovach, L. H., Van Ness, H. C., *J. Chem. Eng. Data*, **11**, 40 (1966).
(12) Stokes, R. H., Marsh, K. N., Tomlins, R. P., *J. Chem. Thermodyn.*, **1**, 211 (1969).
(13) Wilson, G. M., *J. Am. Chem. Soc.*, **86**, 127 (1964).
(14) Winterhalter, D. R., Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, N.Y., 1965.
(15) Winterhalter, D. R., Van Ness, H. C. *J. Chem. Eng. Data*, **11**, 189 (1966).

Received for review June 29, 1977. Accepted December 16, 1977. The financial support of Phillips Petroleum Co. and of the National Science Foundation is gratefully acknowledged.