Table II. Vapor–Liquid Equilibrium Data for Methane + *n*-Hexadecane

p, atm	x_M	y_M	K_M	K_{HD}
		189.3 °C		
20.02	0.0801	0.995 44	12.43	0.004 96
30.71	0.1187	0.996 58	8.40	0.003 88
49.8	0.1824	0.997 22	5.47	0.003 40
100.0	0.3207	0.997 18	3.11	0.004 15
149.9	0.4326	0.996 36	2.30	0.006 42
200.9	0.5193	0.994 67	1.92	0.011 09
249.3	0.5958	0.992 06	1.67	0.019 64
		269.5 °C		
20.50	0.0831	0.958 0	11.53	0.045 8
30.23	0.1208	0.968 7	8.02	0.035 6
50.0	0.1884	0.976 5	5.18	0.029 0
99.5	0.3322	0.980 8	2.95	0.028 8
149.9	0.4539	0.979 8	2.16	0.037 0
200.6	0.5512	0.975 4	1.77	0.054 8
222.5	0.6229	0.971 9	1.56	0.074 5
		350.0 °C		
20.71	0.0836	0.793 0	9.49	0.226
31.39	0.1265	0.845 3	6.68	0.177 1
50.0	0.2032	0.886 5	4.36	0.142 4
99.7	0.3716	0.913 2	2.46	0.138 1
150.3	0.5178	0.909 7	1.76	0.187 3
176.1	0.5968	0.897 0	1.50	0.256
201.3	0.7371	0.873 3	1.18	0.482
		430.4 °C		
20.87	0.0697	0.309 7	4.44	0.742
30.77	0.1363	0.463 2	3.40	0.622
49.8	0.2822	0.509 9	1.81	0.683

co-workers at 350 °C. This is the highest temperature reported by Sultanov et al. and is the only temperature at which their study and ours coincide. The data shown in Figure 4 are read from their graph. The agreement with our data seems reasonable.

Acknowledgment

Dr. J. J. Simnick and Dr. G. D. Nageshwar assisted in the measurements.

Glossary

K	vaporization equilibrium ratio = y/x
p	pressure, atm
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase

Subscripts

H	hydrogen
HD	*n*-hexadecane
M	methane

Literature Cited

(1) Chappelow, C. C.; Prausnitz, J. M. *AIChE J.* **1974**, *20*, 1097.
(2) Sebastian, H. M.; Yao, J.; Lin, H. M.; Chao, K. C. *J. Chem. Eng. Data* **1978**, *23*, 167.
(3) Simnick, J. J., Lawson, C. C.; Lin, H. M.; Chao, K. C. *AIChE J.* **1977**, *23*, 469.
(4) Simnick, J. J.; Liu, K. D.; Lin, H. M.; Chao, K. C. *Ind. Eng. Chem. Process Des. Develop.* **1978**, *17*, 204.
(5) Sultanov, R. G.; Skripka, V. G.; Namiot, A., Yu. *Gazov. Delo* **1972**, *10*, 43.
(6) Yao, J.; Sebastian, H. M.; Lin, H. M.; Chao, K. C. *Fluid Phase Equilibria* **1978**, *1*, 293.

Received for review December 7, 1979. Accepted March 7, 1980. Funds for this study were provided by the Electric Power Research Institute through Research Project RP-367.

Excess Thermodynamic Functions for Ternary Systems. 6. Total-Pressure Data and G^E for Acetone–Ethanol–Water at 50 °C

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Isothermal P–x data for the ternary system acetone–ethanol–water at 50 °C are reported, together with data for the constituent binaries. Data reduction by Barker's method provides a correlation for G^E.

The VLE measurements reported here are for the acetone (1)–ethanol (2)–water (3) system at 50 °C. Experimental values of total vapor pressure are presented for the full composition range of the three constituent binaries and for six runs on ternary mixtures formed by additions of each pure species to mixtures of the other two in molar proportions of approximately 2 to 1. The apparatus is that of Gibbs and Van Ness (*8*) as modified by DiElsi et al. (*7*).

The acetone was chromatoquality reagent from Matheson Coleman and Bell; the reagent-grade ethanol was supplied by U.S. Industrial Chemicals, and the water was doubly deionized. Except for being degassed, all reagents were used as received, with indicated purities of at least 99.8 mol %. Vapor pressures of the pure constituents measured in this work and comparable values from the literature are reported in Table I. The P_i^{sat} values in all calculations are fixed at averages of our experimental measurements.

Table I. Vapor Pressures of Pure Species at 50 °C in kPa

	acetone (1)	ethanol (2)	water (3)
present work	82.029	29.484	12.355
	82.029	29.515	12.375
	82.015	29.490	12.331
	82.000	29.493	12.358
av value	82.018	29.496	12.355
lit. values	81.989 (*7*)	29.494 (*4*)	12.345 (*3, 11*)
	81.835 (*6*)	29.481 (*11*)	12.350 (*12*)
		29.493 (*12*)	12.347 (*5*)
		29.472 (*5*)	12.349 (*10*)

Results and Correlations

Tables II–IV give experimental values of total pressures for the three constituent binaries, and Table V contains all data for

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Table II. Total Pressure Data for Acetone (1)-Ethanol (2) at 50 °C

x_1	x_2	P, kPa	x_1	x_2	P, kPa
0.0000	1.0000	29.484	0.5062	0.4938	66.347
0.0532	0.9468	36.484	0.5853	0.4147	69.426
0.1009	0.8991	41.620	0.6526	0.3474	71.842
0.1759	0.8241	48.173	0.7318	0.2682	74.467
0.3380	0.6620	58.577	0.8146	0.1854	77.019
0.4072	0.5928	62.032	0.8873	0.1127	79.160
0.4880	0.5120	65.612	0.9422	0.0578	80.620
			1.0000	0.0000	82.029

Table III. Total Pressure Data for Acetone (1)-Water (2) at 50 °C

x_1	x_2	P, kPa	x_1	x_2	P, kPa
0.0000	1.0000	12.355	0.3977	0.6023	68.842
0.0290	0.9710	30.048	0.4902	0.5098	70.809
0.0484	0.9516	38.121	0.5909	0.4091	72.858
0.0732	0.9268	45.659	0.6918	0.3082	74.998
0.0977	0.9023	50.931	0.7945	0.2055	77.437
0.1476	0.8524	57.769	0.8972	0.1028	79.972
0.1996	0.8004	61.870	0.9481	0.0519	81.111
0.2985	0.7015	66.199	0.9796	0.0204	81.702
			1.0000	0.0000	82.029

Table IV. Total Pressure Data for Ethanol (1)-Water (2) at 50 °C

x_1	x_2	P, kPa	x_1	x_2	P, kPa
0.0000	1.0000	12.375	0.4987	0.5013	27.646
0.0220	0.9780	15.087	0.4765	0.5235	27.458
0.0490	0.9510	17.640	0.5236	0.4764	27.828
0.0743	0.9257	19.614	0.5769	0.4231	28.213
0.1008	0.8992	21.142	0.6269	0.3731	28.541
0.1505	0.8495	23.081	0.6756	0.3244	28.824
0.1995	0.8005	24.242	0.7253	0.2747	29.072
0.2491	0.7509	25.073	0.7753	0.2247	29.299
0.2999	0.7001	25.728	0.8337	0.1663	29.474
0.3480	0.6520	26.257	0.8862	0.1138	29.567
0.3991	0.6009	26.759	0.9434	0.0566	29.576
0.4487	0.5513	27.216	1.0000	0.0000	29.515

the six runs made with ternary mixtures. Data reduction is by Barker's method according to procedures described earlier (*1*, *2*). For all three binary systems the analytical expression for G^E is provided by the Margules equation

$$g_{ij} \equiv G^E{}_{ij}/RT = [A_{ji}x_i + A_{ij}x_j - (\lambda_{ji}x_i + \lambda_{ij}x_j)x_ix_j + (\eta_{ji}x_i + \eta_{ij}x_j)(x_ix_j)^2]x_ix_j \quad (1)$$

For the ethanol (2)-water (3) system, the correlation requires values for all six parameters in eq 1; however, for acetone (1)-water (3), $\eta_{31} = \eta_{13}$, and for acetone (1)-ethanol (2), $\eta_{21} = \eta_{12} = 0$.

The ternary data are well fit by the following form of the Wohl equation

$$g_{123} = g_{12} + g_{13} + g_{23} + (C_0 + C_1x_1 + C_2x_2)x_1x_2x_3 \quad (2)$$

Correlations for the g_{ij} are provided by eq 1; parameters C_0, C_1, and C_2 are found by regression of just the ternary data.

Second virial coefficients B_{ij} required to account for vapor-phase nonidealities are estimated by the method of Hayden and O'Connell (*9*).

Results of the correlations of data for the binary systems, together with all ancillary information, are summarized in Table VI. Correlation of the data for ternary mixtures, with binary parameters fixed at the values given in Table VI, yields the following values for the ternary parameters:

$$C_0 = 1.866 \pm 0.019$$

$$C_1 = 1.186 \pm 0.022$$

$$C_2 = 0.901 \pm 0.036$$

The RMS (root-mean-square) of ΔP for the ternary data is 0.047 kPa; the maximum $|\Delta P|$ is 0.119 kPa.

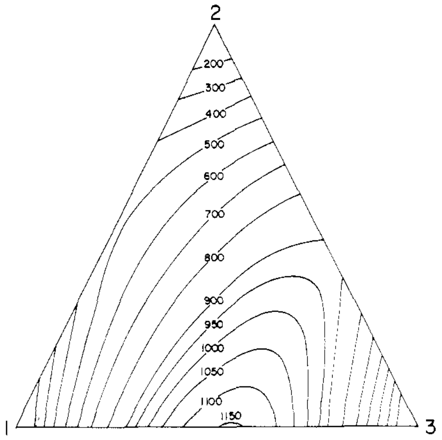

Figure 1. Lines of constant G^E (J/mol) for the acetone (1)-ethanol (2)-water (3) system at 50 °C.

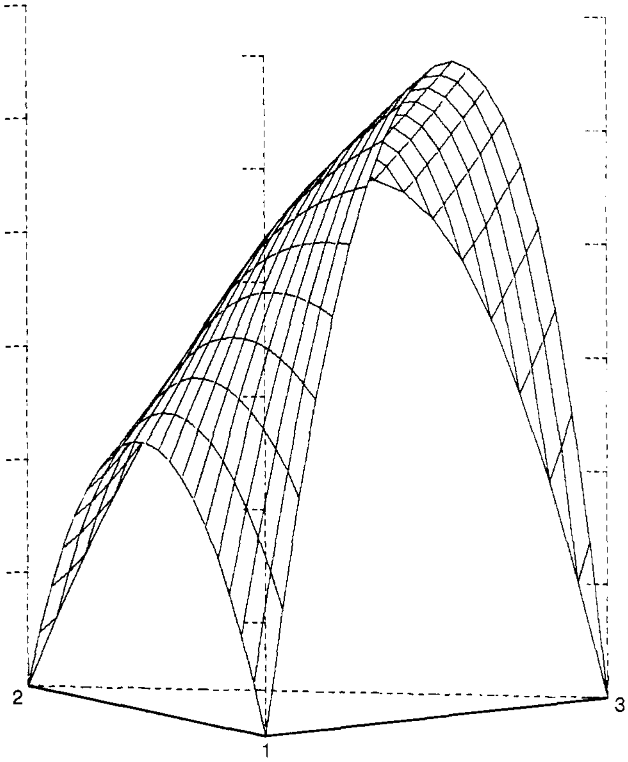

Figure 2. Pictorial view of the G^E-x surface for the acetone (1)-ethanol (2)-water (3) system at 50 °C.

Discussion

No previous work directly comparable with ours appears in the literature for the ternary system or for the acetone-ethanol and acetone-water binary systems. For ethanol-water the standard of comparison is the work of Pemberton and Mash (*11*), whose data set at 50 °C is almost as well correlated by our equation for G^E as is our own data set. The RMS of ΔP is 0.036

Table V. Total Pressure Data for Acetone (1)-Ethanol (2)-Water (3) at 50 °C

x_1	x_2	x_3	P, kPa
0.0000	1.0000	0.0000	29.490
0.0000	0.6760	0.3240	28.776
0.0540	0.6395	0.3065	35.339
0.1089	0.6024	0.2887	41.030
0.1624	0.5662	0.2714	45.962
0.2154	0.5304	0.2542	50.260
0.2618	0.4990	0.2392	53.648
0.3087	0.4674	0.2239	56.712
0.3565	0.4350	0.2085	59.509
0.4045	0.4026	0.1929	62.053
0.4546	0.3687	0.1767	64.470
0.5053	0.3344	0.1603	66.721
0.0000	0.0000	1.0000	12.358
0.0000	0.3041	0.6959	25.761
0.0544	0.2876	0.6580	34.807
0.1080	0.2713	0.6207	41.718
0.1604	0.2554	0.5842	47.295
0.2127	0.2395	0.5478	51.886
0.3141	0.2087	0.4772	58.900
0.3627	0.1939	0.4434	61.607
0.4126	0.1788	0.4086	64.067
0.4610	0.1640	0.3750	66.194
0.5098	0.1492	0.3410	68.159
1.0000	0.0000	0.0000	82.015
0.6604	0.0000	0.3396	74.301
0.6225	0.0574	0.3201	72.569
0.5902	0.1065	0.3033	71.092
0.5581	0.1551	0.2868	69.588
0.5258	0.2040	0.2702	68.059
0.4938	0.2525	0.2537	66.472
0.4619	0.3007	0.2374	64.949
0.4271	0.3535	0.2194	63.165
0.3945	0.4028	0.2027	61.441
0.3625	0.4513	0.1862	59.756
0.3306	0.4996	0.1698	57.986
0.0000	0.0000	1.0000	12.331
0.2928	0.0000	0.7072	65.962
0.2776	0.0524	0.6700	62.259
0.2627	0.1037	0.6336	59.074
0.2487	0.1519	0.5994	56.496
0.2344	0.2010	0.5646	54.195
0.2200	0.2502	0.5298	52.166
0.2052	0.3008	0.4940	50.313
0.1908	0.3499	0.4593	48.660
0.1759	0.4011	0.4230	47.095
0.1609	0.4522	0.3869	45.648
0.1461	0.5026	0.3513	44.291
0.0000	1.0000	0.0000	29.493
0.2971	0.7029	0.0000	56.258
0.2826	0.6687	0.0487	55.299
0.2677	0.6334	0.0989	54.238
0.2525	0.5975	0.1500	53.077
0.2378	0.5628	0.1994	51.945
0.2228	0.5272	0.2500	50.761
0.2068	0.4893	0.3039	49.514
0.1920	0.4543	0.3537	48.347
0.1773	0.4194	0.4033	47.244
0.1624	0.3841	0.4535	46.120
0.1478	0.3497	0.5025	45.051
1.0000	0.0000	0.0000	82.000
0.7010	0.2990	0.0000	73.473
0.5896	0.2515	0.1589	70.094
0.5526	0.2357	0.2117	68.863
0.5195	0.2216	0.2589	67.732
0.4848	0.2068	0.3084	66.561
0.4500	0.1920	0.3580	65.377
0.4158	0.1774	0.4068	64.212
0.3809	0.1625	0.4566	63.053
0.3463	0.1478	0.5059	61.875

Table VI. Summary of Results for Binary Systems at 50 °C[a]

	acetone (1)-ethanol (2)	acetone (1)-water (3)	ethanol (2)-water (3)
P_i^{sat}, kPa	82.018	82.018	29.496
P_j^{sat}, kPa	29.496	12.355	12.355
V_i^L, cm^3/mol	76.92	76.92	60.36
V_j^L, cm^3/mol	60.36	18.23	18.23
B_{ii}, cm^3/mol	−1440	−1440	−1400
B_{jj}, cm^3/mol	−1400	−1140	−1140
B_{ij}, cm^3/mol	−1210	−870	−1170
A_{ij}	0.7815 ± 0.0023	2.2780 ± 0.0016	1.5971 ± 0.0070
A_{ji}	0.6784 ± 0.0018	1.7325 ± 0.0042	0.9407 ± 0.0148
λ_{ij}	0.1578 ± 0.0106	1.3464 ± 0.0169	−0.3925 ± 0.0748
λ_{ji}	0.0531 ± 0.0091	0.6865 ± 0.0315	0.4235 ± 0.1598
η_{ij}		0.6469 ± 0.0570	−2.2393 ± 0.2226
η_{ji}		0.6469 ± 0.0570	1.0680 ± 0.4265
RMS ΔP, kPa	0.012	0.021	0.015
max $\lvert\Delta P\rvert$, kPa	0.023	0.036	0.049

[a] Pairs of components are listed in the order i, j.

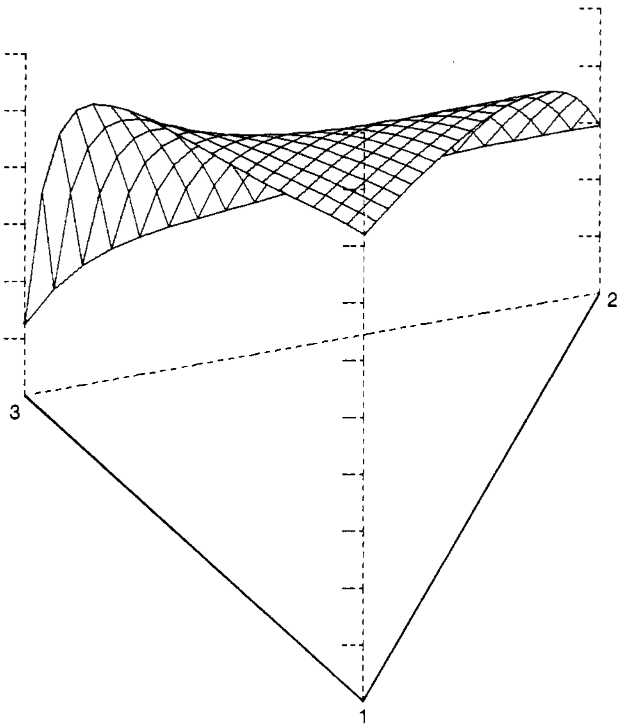

Figure 3. Pictorial view of the P–x surface for the acetone (1)–ethanol (2)–water (3) system at 50 °C.

kPa and the max $|\Delta P|$ is 0.079 kPa. This excellent agreement is particularly gratifying because our earlier results for this system (*5*, *12*) in comparison with those of Pemberton and Mash showed pressure differences of up to 0.3 kPa. Minor modifications in experimental technique are responsible for the improved results reported here.

The results of this study are displayed pictorially by Figures 1-3. Figure 1 is a contour diagram showing lines of constant G^E on a triangular grid of mole fractions. Figure 2 is an oblique view of the same surface, and Figure 3 is a similar view of the P–x surface. There is no ternary azeotrope and but a single binary azeotrope, for ethanol–water at $x_{ethanol}$ = 0.9318 and P^{az} = 29.588 kPa.

Glossary

A_{ij}, A_{ji}	parameters in eq 1
B_{ij}	second virial coefficient
C_0, C_1, C_2	parameters in eq 2

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G^E	excess Gibbs function, liquid phase
g	G^E/RT
P	total pressure
P_i^{sat}	vapor pressure of pure i
R	universal gas constant
T	absolute temperature
V_i^L	molar volume of pure liquid i
x	mole fraction, liquid phase

Greek Letters

λ_{ij}, λ_{ji}	parameters in eq 1
η_{ij}, η_{ji}	parameters in eq 1
Δ	signifies a difference

Literature Cited

(1) Abbott, M. M., Floess, J. K., Walsh, G. E., Van Ness, H. C., *AIChE J.*, **21**, 72 (1975).

(2) Abbott, M. M., Van Ness, H. C., *AIChE J.*, **21**, 62 (1975).

(3) Ambrose, D., Lawrenson, I. J., *J. Chem. Thermodyn.*, **4**, 755 (1972).

(4) Ambrose, D., Sprake, C. H. S., Townsend, R., *J. Chem. Thermodyn.*, **7**, 185 (1975).

(5) Balcázar-Ortiz, A. M., Patel, R. B., Abbott, M. M., Van Ness, H. C., *J. Chem. Eng. Data*, **24**, 133 (1979).

(6) Diaz Pena, M., Crespocolin, A., Compostizo, A., *J. Chem. Thermodyn.*, **10**, 1101 (1978).

(7) DiElsi, D. P., Patel, R. B., Abbott, M. M., Van Ness, H. C., *J. Chem. Eng. Data*, **23**, 242 (1978).

(8) Gibbs, R. E., Van Ness, H. C., *Ind. Eng. Chem. Fundam.*, **11**, 410 (1972).

(9) Hayden, J. G., O'Connell, J. P., *Ind. Eng. Chem. Process Des. Dev.*, **14**, 209 (1975).

(10) Keenan, J. H., Keyes, F. G., Hill, P. G., Moore, J. G., "Steam Tables", Wiley, New York, 1969.

(11) Pemberton, R. C., Mash, C. J., *J. Chem. Thermodyn.*, **10**, 867 (1978).

(12) Wilson, S. R., Patel, R. B., Abbott, M. M., Van Ness, H. C., *J. Chem. Eng. Data*, **24**, 130 (1979).

Received for review December 31, 1979. Accepted April 7, 1980. Partial support for this work came from National Science Foundation Grant No. ENG78-10048.

Solubilities of Phenol and Chlorinated Phenols in Supercritical Carbon Dioxide

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Solubilities of phenol, *p*-chlorophenol, and 2,4-dichlorophenol in supercritical carbon dioxide were measured at 36 °C over a range of pressures from 80 to 250 atm. The solubility of phenol in supercritical carbon dioxide was also measured at 60 °C over the same pressure range. The data represent the effects of pressure and temperature on solubility as well as solubility trends in an homologous series of compounds.

Introduction

Recent applications in high-pressure dense-gas extraction processes—such as coffee decaffeination (*1*) and regeneration of activated carbon (*2*)—have led to an increasing interest in this separation process, which is based upon the ability to vary the solvent power of a fluid in the vicinity of its critical point with small changes in temperature and/or pressure. Supercritical carbon dioxide (T_c = 31 °C; P_c = 72.8 atm) appears to be the preferred solvent in the above processes, primarily because carbon dioxide is environmentally acceptable, inexpensive, and readily available. There are, however, very little experimental data for solubilities in supercritical carbon dioxide, especially as a function of temperature and pressure. Francis (*3*) has measured solubilities in liquid carbon dioxide for a large number of solutes but only at a single temperature and pressure—saturated carbon dioxide at 25 °C. Tsekhanskaya et al. (*4*) measured the solubility of solid naphthalene in supercritical carbon dioxide at three different temperatures and over a range of pressures. The data illustrate the large solubility enhancement, which results when compressing gaseous carbon dioxide to supercritical fluid densities, and the dramatic sensitivity of solubility as a function of temperature and pressure in the critical region of the solvent. As a preliminary study in our work investigating the use of supercritical carbon dioxide for regenerating activated carbon, we have measured the solubilities of three common waste-water pollutants—phenol, *p*-chlorophenol, and 2,4-dichlorophenol—in supercritical carbon dioxide as a function of pressure.

Experimental Section

A schematic diagram of the experimental apparatus for measuring solubilities is given in Figure 1. Liquid carbon dioxide (Linde "bone dry") at ambient temperatures is charged into a Milton Roy high-pressure liquid pump and compressed to the desired pressure. The pump is used to continuously deliver solvent at flow rates from 60 to 300 standard cm^3/min and at constant pressures up to 250 atm. Preliminary experiments were accomplished at flow rates up to 500 cm^3/min with no effect on the measured solubilities. After reaching thermal equilibrium within the constant-temperature bath (controlled by a Sargent-Welch Thermonitor), the solvent is fed into the first of two high-pressure equilibrium cells (High Pressure Equipment, Inc.) connected in series. The solvent migrates slowly through the column—packed with glass beads and the heavy solute—becoming saturated with the solute prior to exiting the second column. Entrainment of the solute is prevented by inserting glass wool plugs at the top of each packed column. Once the saturated solution exits the second cell, it is flashed to atmospheric pressure across a heated metering valve (Whitey Co.) and the heavy component is collected in a cold trap held at ice temperature. The amount collected is determined by weighing, and the corresponding volume of carbon dioxide is measured with a wet-test meter. The equilibrium pressure is measured at the exit of the second column with a Bourdon-type Heise pressure gauge (0–5000 psi range). Fluctuations in pressure due to the high-pressure liquid pump are less than ±25 psi over the entire pressure range. Temperature is measured to within 1 °C with

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