J. Chem. Eng. Data 1983, 28, 218-223

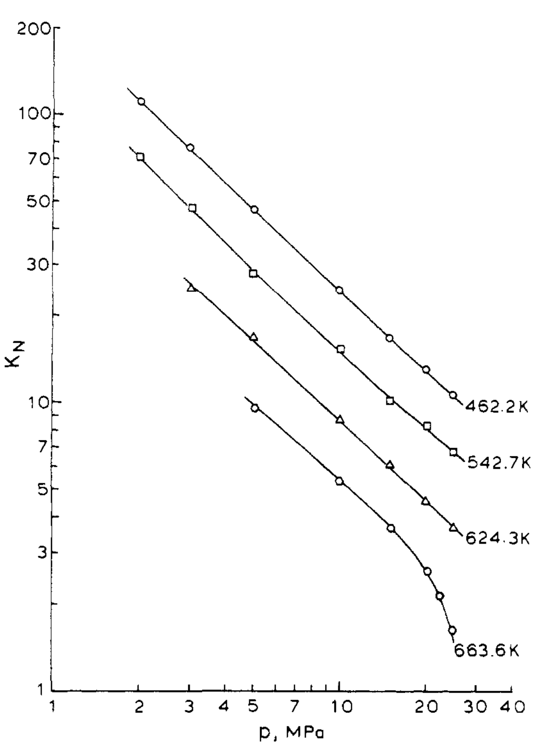

Figure 3. *K* value of nitrogen in nitrogen + *m*-cresol.

Subscripts

Cr	*m*-cresol
N	nitrogen
T	Tetralin

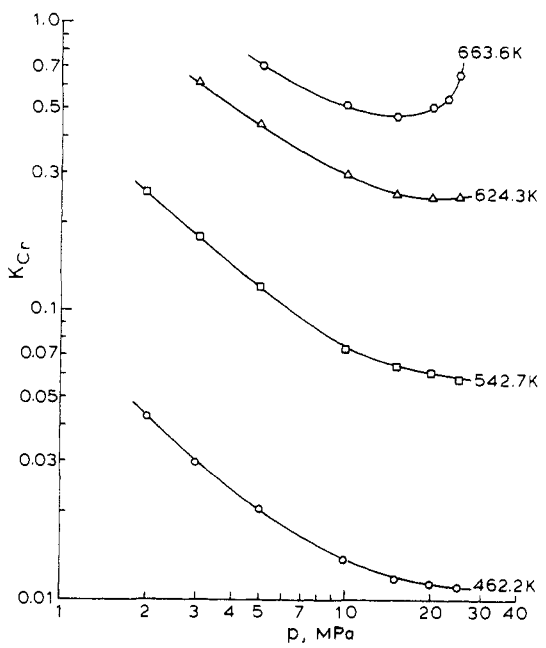

Figure 4. *K* value of *m*-cresol.

Registry No. Nitrogen, 7727-37-9; Tetralin, 119-64-2; *m*-cresol, 108-39-4.

Literature Cited

(1) Simnick, J. J.; Lawson, C. C.; Lin, H. M.; Chao, K. C. *AIChE J.* **1977**, *23*, 469-76.

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Equation of State and Thermodynamic Properties of Liquid Methanol from 298 to 489 K and Pressures to 1040 bar

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The *PVT* properties of liquid methanol have been measured with a direct-weighing *PVT* apparatus, from 298 to 489 K and pressures to 1040 bar. The apparatus and the method are described. The results have been fitted to a 16-constant equation of state that has been used, together with published data for vapor pressure and saturated-vapor densities, to calculate the following properties of saturated and compressed liquid methanol over the experimental range: specific volume, isothermal compressibility, thermal expansion coefficient, thermal pressure coefficient, enthalpy, entropy, and constant-pressure heat capacity. The calculated properties are presented in tabular form, at round values of *P* and *T*.

Introduction

World demand for methanol, at about 12 × 10^6 t in 1980, is expected to soar to 48 × 10^6 t by the end of the century. New markets will account for most of the increase, with the Mobil Corp.'s methanol-to-gasoline conversion process the largest potential consumer.

Existing sources of thermodynamic properties of methanol are few and scattered (*1–10*). Figure 1 shows the pressure–temperature regions covered by previous *PVT* experiments, as well as that covered by this work. A preliminary analysis of the earlier *PVT* measurements suggests that only those of Zubarev and Bagdonas (*7*) and Ta'ani (*3*) are of suitable accuracy for constructing an equation of state (*11*). In this work (*12*) we have measured the *PVT* properties of liquid methanol at 167 points, including seven isotherms from 298 to 489 K (25–216 °C) and pressures from saturation to about 1000 bar; this covers a wide region that has not previously been studied, and overlaps with the two most accurate recent studies (*3*, *7*) so that comparisons can be made.

Our *PVT* data have been fitted to a 16-constant equation of state which has been used to calculate, at regular intervals of pressure and temperature, the following properties of compressed liquid methanol: specific volume, isothermal compressibility, thermal expansion coefficient, thermal pressure

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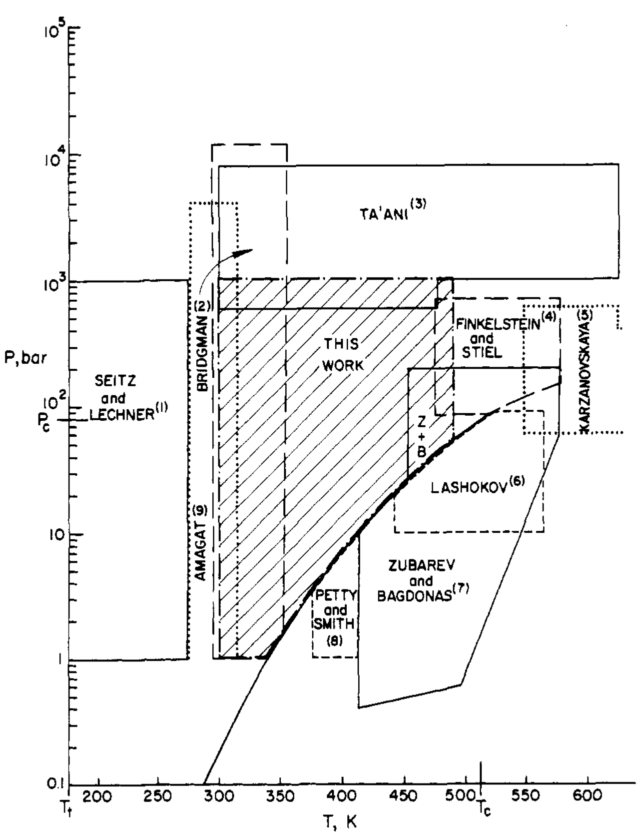

Figure 1. Regions of pressure–temperature space covered in this work and previous experiments.

coefficient, enthalpy, entropy, and heat capacity at constant pressure. The equation of state, together with published values of vapor pressure, has been used to calculate the following properties of the saturated liquid: specific volume, enthalpy of vaporization, isothermal compressibility, thermal expansion coefficient, and thermal pressure coefficient.

Experimental Section

Apparatus. A new, direct-weighing *PVT* apparatus was constructed and used for this work (Figure 2). In this apparatus a pressure cell of known volume is suspended from an electronic balance by stainless-steel capillary tubing that is connected to a pressure generator and a dead-weight gauge. A differential-pressure null indicator (not shown in the figure) separates the methanol from the oil that serves as the pressure medium in the dead-weight gauge. The pressure cell hangs inside an air-filled copper vessel immersed in a stirred oil bath that is maintained at constant temperature (±0.02 K) by a proportional temperature controller. Temperatures are measured by a platinum resistance thermometer suspended near the middle of the pressure cell, but not touching it. Two thermocouples, referenced to the resistance thermometer, are used to measure temperatures at the top and bottom of the copper vessel, to ensure that no significant temperature gradients exist when weight measurements are recorded.

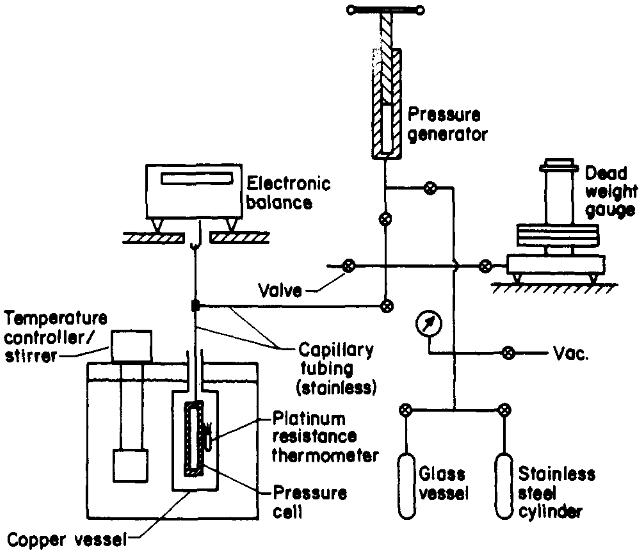

Figure 2. Diagram of experimental apparatus.

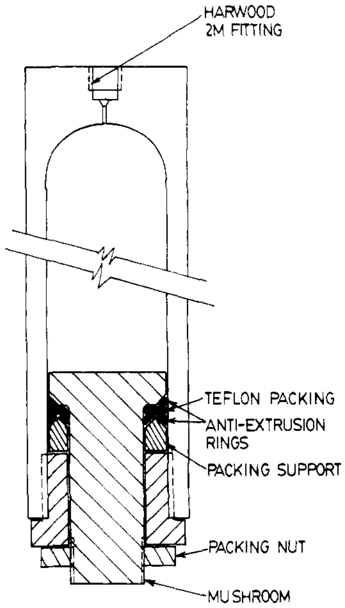

Figure 3. Schematic diagram showing details of cell closure. The cell was suspended by stainless-steel capillary tubing (0.030-in. o.d. × 0.018-in. i.d.) connected by a Harwood Co. type 2M fitting to the opening at the top of the cell.

The pressure cell (Figure 3) was machined from Vascomax 300 maraging steel (yield strength ≃ 250 kpsi). Its inside and outside diameters are 1.125 and 1.5 in. and its overall length is about 7.5 in., giving it an internal volume of about 82 cm^3. The precise volume at 298.15 K and 1 atm was determined by comparing our measurements for methanol to the known density under those conditions (0.786 63 g/cm^3) (*10*); the volume was found to be 82.41 ± 0.04 cm^3 (*16*). The cell is fitted with a Bridgman-type unsupported area closure, using a 1/16-in. thick Teflon packing. The mass of the empty cell, including the capillary suspension system, was about 1065 g, and the mass of methanol in the cell during measurements ranged from about 42 to 70 g. A Mettler Model PL 1200 electronic balance was used; it has a maximum capacity of 1200 g and a precision of ±0.01 g. Through repeated pressure and temperature cycling, we found the total mass at fixed pressure and temperature to be reproducible to within about ±0.02 g, which corresponds to a precision in methanol density measurement of ±0.05% or better. The electronic balance measures the restoring force necessary to support the weighing mechanism in a fixed position; hence, there is no vertical motion of the cell during weighing.

The principal corrections applied to the raw measurements to obtain methanol densities are as follows: (1) the mass of methanol in the capillary tubing from which the cell is suspended (approximately 0.1 g); (2) the change in the volume of the cell with pressure and temperature; and (3) changes in the buoyant force of air on the cell with changes in temperature. Changes in the cell volume with pressure were calculated from standard elasticity theory (*17*) in two parts: (a) the expansion of a thick-walled cylinder, closed at one end; (b) the compression

Table I. Measured Specific Volumes (cm^3/g) for Liquid Methanol

	T/K										
P/bar	298.12	322.54	342.83	362.90	382.60	402.34	421.61	441.90	463.06	478.62	488.86
5.14	1.2706	1.3090	1.3455	1.3847							
12.03	1.2696	1.3078	1.3435	1.3829	1.4260	1.4785					
18.92	1.2685	1.3066	1.3420	1.3809	1.4238	1.4757					
32.97	1.2663	1.3038	1.3387	1.3770	1.4191	1.4694	1.5290	1.6113			
53.83	1.2632	1.2999	1.3343	1.3715	1.4122	1.4605	1.5169	1.5933	1.7057	1.8332	1.9762
66.47	1.2612	1.2978	1.3313	1.3681	1.4081	1.4554	1.5102	1.5829	1.6904	1.8029	1.9174
101.08	1.2565	1.2921	1.3244	1.3594	1.3976	1.4428	1.4935	1.5598	1.6522	1.7445	1.8276
149.78			1.3156	1.3491	1.3845	1.4265	1.4736	1.5335	1.6129	1.6856	1.7455
218.72	1.2416	1.2739	1.3037	1.3350	1.3681	1.4066	1.4489	1.5008	1.5678	1.6262	1.6734
280.92	1.2342	1.2654	1.2939	1.3234	1.3547	1.3909	1.4304	1.4778	1.5367	1.5869	1.6271
353.66	1.2261	1.2557	1.2830	1.3108	1.3404	1.3746	1.4103	1.4538	1.5064	1.5508	1.5855
424.61	1.2182	1.2475	1.2732	1.3002	1.3282	1.3602		1.4337	1.4819	1.5215	1.5517
487.29	1.2117	1.2404	1.2651	1.2905	1.3178	1.3489	1.3798	1.4180	1.4613	1.4980	1.5272
625.06	1.1992	1.2261	1.2488	1.2726	1.2974	1.3253	1.3538	1.3876	1.4270	1.4575	1.4817
762.84	1.1879	1.2131	1.2345	1.2568	1.2797	1.3053	1.3318	1.3620	1.3971	1.4249	1.4460
900.63	1.1775	1.2015	1.2216	1.2425	1.2641	1.2878	1.3124	1.3402	1.3726	1.3975	1.4161
1038.43	1.1682	1.1909	1.2100	1.2299	1.2502	1.2726	1.2958	1.3216	1.3513	1.3741	1.3909

of those portions of the seal assembly exposed to approximately hydrostatic pressure. The former accounted for 80% and the latter 20% of the total pressure correction, which was calculated to be 4.6×10^{-4} cm^3/bar. The maximum buoyancy correction was about 0.1 g. The absolute accuracy of the reported density measurements is estimated to be ±0.1%, and the reproducibility is ±0.05% or better.

Temperatures were measured on IPTS68 with a platinum resistance thermometer and Mueller temperature bridge and are estimated to be accurate to within ±0.05 K. Pressures were measured by a Ruska dead-weight gauge and are accurate to within ±0.02%.

Methanol with an initial minimum purity of 99.98% was used. It was double distilled after being dehydrated by using molecular sieves.

Further details of the construction and calibration of the apparatus can be found in the thesis of Machado (*12*).

Procedure. Before each series of experiments was begun, the system was flushed with pure methanol and pumped down for at least 24 h with a vacuum pump, while the temperature was set at 100 °C. The weight of the empty vessel was then recorded, and methanol was added by distilling it from the stainless-steel cylinder into the evacuated system. After the temperature stabilized at the desired value, pressure was applied by means of the hand-operated pressure generator and measured by the dead-weight gauge. The work done by compression or expansion of the liquid in the pressure cell caused a change in temperature, and time was allowed for it to return to its preset value (usually about 0.5 h). After the temperature and pressure had remained stable for 15–30 min, the weight and the pressure were recorded, and the pressure was changed to the next value. Duplicate weight measurements were recorded with increasing and decreasing pressure, and these agreed to within ±0.02 g.

Results and Comparisons

The experimental *PVT* measurements are recorded in Table I. Because of the ease with which pressure can be adjusted in the apparatus, measurements were made at the same pressures at each temperature.

Our *PVT* results overlap those reported by several other scientists (see Figure 1); however, we have made careful comparisons only with the recent measurements of Ta'ani (*3*) and Zubarev and Bagdonas (*7*). Ta'ani measured densities only at high pressures, from 500 to 8000 bar. A comparison at 15 selected points at pressures from 500 to 1000 bar and temperatures from 298 to 473 K, showed a maximum difference of 0.52% in density, and an average absolute difference of 0.24%. The differences, plotted in Figure 4, suggest that in the range of overlap the two sets of data exhibit different trends with both temperature and pressure, although the average difference is within the combined uncertainities of the two experiments. For the four experimental points of Zubarev and Bagdonas that overlap our work there is an average difference of 0.32% in density; however, the number of points is insufficient to draw any conclusions about systematic differences. A cursory comparison with the measurements of Amagat (*9*), carried out before the turn of the century, shows that his densities agree with ours to within about 0.35%.

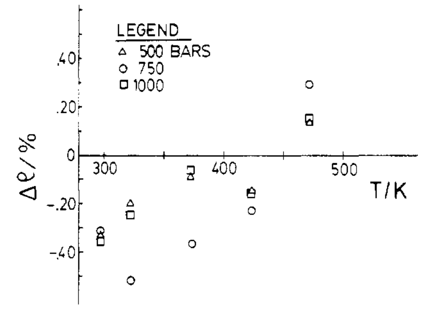

Figure 4. Differences between this work and the measurements of Ta'ani (*3*). $\Delta\rho \equiv (\rho_T - \rho)(100/\rho)$, where ρ_T is the density reported by Ta'ani (*3*) and ρ is the density calculated from eq 1.

Equation of State for Liquid Methanol

The *PVT* data in Table I, together with saturated-liquid densities obtained by graphical extrapolations of our isotherms to saturation pressures, have been fitted to a 16-constant equation of state proposed by Zubarev et al. (*10*):

$$P = B(T)\rho + C(T)\rho^2 + D(T)\rho^3 + E(T)\rho^4 + F(T)\rho^5 \quad (1)$$

where

$$B(T) = \sum_{i=0}^{4} a_i \tau^i$$

$$C(T) = \sum_{i=0}^{3} a_{i+5} \tau^i$$

$$D(T) = \sum_{i=1}^{3} a_{i+8} \tau^i$$

$$E(T) = \sum_{i=1}^{2} a_{i+11} \tau^i$$

$$F(T) = \sum_{i=1}^{2} a_{i+13} \tau^i$$

$$\tau = 1000/T$$

Table II. Constants for Eq 1 Obtained by Least-Squares Method[a]

$a_0 = 0.30715587 \times 10^5$
$a_1 = -0.72122933 \times 10^5$
$a_2 = 0.40221454 \times 10^5$
$a_3 = -0.65735159 \times 10^4$
$a_4 = 0.68311164 \times 10^2$
$a_5 = -0.81069326 \times 10^4$
$a_6 = 0.15280382 \times 10^6$
$a_7 = -0.89207642 \times 10^5$
$a_8 = 0.11034779 \times 10^5$
$a_9 = -0.24725760 \times 10^6$
$a_{10} = 0.11738188 \times 10^6$
$a_{11} = -0.53049022 \times 10^4$
$a_{12} = 0.23281053 \times 10^6$
$a_{13} = -0.10283530 \times 10^6$
$a_{14} = -0.77954836 \times 10^5$
$a_{15} = 0.38600697 \times 10^5$

[a] Pressure is in bar, density (ρ) in g/cm^3, and temperature in Kelvin.

The 16 constants determined by using a weighted linear least-squares method (*13*) are recorded in Table II. The weighting function used compensates for large variations in the slopes of the isotherms (i.e., in the isothermal compressibilities) that are observed in these measurements. The effect of the weighting function is equivalent to minimizing the sum of the squared perpendicular distances from the fitted surface to the data points in a linear space in which the variances of the variables are equal (*13*). The maximum difference between observed densities and those calculated from eq 1 was found to be 0.19%, and the average absolute difference for all 178 fitted points was 0.03%. Equation 1 can be solved for density at fixed P and T by iterative methods, and the results will be in good agreement with experimental data. The equation is less suitable for calculating T at fixed ρ and P, because the large value of $(\partial P/\partial \rho)_T$ ($\simeq$800 bar cm^3/g) and the inherent scatter in ρ ($\simeq 3 \times 10^{-4}$ g/cm^3) lead to errors of the order of 2.4 bar in pressure, a relatively large value in the low pressure range.

Values of the specific volume of liquid methanol at round values of pressure and temperature, calculated from eq 1, are recorded in Table III.

Table III. Specific Volume (cm^3/g) of Liquid Methanol at Round Values of Pressure and Temperature from Eq 1

	T/K									
P/bar	298.15	313.15	333.15	353.15	373.15	393.15	413.15	433.15	453.15	473.15
1	1.2710	1.2946	1.3285							
5	1.2703	1.2939	1.3276	1.3647	1.4067					
10	1.2696	1.2930	1.3266	1.3635	1.4051	1.4537				
25	1.2673	1.2905	1.3235	1.3597	1.4005	1.4478	1.5049	1.5779		
50	1.2637	1.2863	1.3185	1.3538	1.3931	1.4385	1.4925	1.5602	1.6513	1.7913
100	1.2567	1.2784	1.3091	1.3425	1.3795	1.4216	1.4708	1.5304	1.6064	1.7100
200	1.2437	1.2638	1.2921	1.3226	1.3559	1.3930	1.4354	1.4847	1.5441	1.6177
300	1.2318	1.2507	1.2771	1.3053	1.3358	1.3694	1.4070	1.4499	1.4999	1.5593
400	1.2210	1.2388	1.2636	1.2900	1.3183	1.3492	1.3833	1.4217	1.4655	1.5162
500	1.2110	1.2279	1.2514	1.2763	1.3028	1.3315	1.3629	1.3979	1.4372	1.4819
600	1.2018	1.2179	1.2403	1.2638	1.2889	1.3158	1.3451	1.3773	1.4131	1.4534
700	1.1933	1.2087	1.2301	1.2525	1.2762	1.3016	1.3291	1.3591	1.3922	1.4291
800	1.1853	1.2001	1.2206	1.2421	1.2647	1.2888	1.3147	1.3429	1.3737	1.4078
900	1.1778	1.1921	1.2118	1.2324	1.2540	1.2770	1.3016	1.3282	1.3571	1.3889
1000	1.1707	1.1845	1.2036	1.2234	1.2442	1.2661	1.2896	1.3148	1.3421	1.3719

Table IV. Isothermal Compressibility, $\beta_T \equiv (-1/V)(\partial V/\partial P)_T \times 10^3$ bar^{-1}, for Liquid Methanol

	T/K									
P/bar	298.15	313.15	333.15	353.15	373.15	393.15	413.15	433.15	453.15	473.15
1	0.120	0.135	0.158							
5	0.119	0.134	0.157	0.186	0.225					
10	0.119	0.133	0.156	0.185	0.223	0.277				
25	0.117	0.131	0.153	0.180	0.216	0.266	0.343	0.479		
50	0.114	0.127	0.148	0.173	0.205	0.250	0.316	0.426	0.640	1.215
100	0.109	0.121	0.139	0.160	0.187	0.223	0.274	0.351	0.481	0.734
200	0.100	0.109	0.123	0.140	0.160	0.185	0.218	0.264	0.331	0.434
300	0.092	0.100	0.111	0.124	0.140	0.159	0.183	0.214	0.257	0.315
400	0.085	0.092	0.101	0.112	0.125	0.140	0.158	0.181	0.211	0.251
500	0.079	0.085	0.093	0.102	0.113	0.125	0.140	0.158	0.180	0.209
600	0.074	0.079	0.086	0.094	0.103	0.113	0.125	0.140	0.158	0.180
700	0.069	0.074	0.080	0.087	0.095	0.103	0.114	0.126	0.141	0.159
800	0.065	0.069	0.075	0.081	0.088	0.095	0.104	0.115	0.127	0.142
900	0.062	0.065	0.070	0.076	0.082	0.089	0.096	0.106	0.116	0.129
1000	0.058	0.062	0.066	0.071	0.077	0.083	0.090	0.098	0.107	0.118

Table V. Thermal Expansion Coefficient, $\alpha_P \equiv (1/V)(\partial V/\partial T)_P \times 10^3$ K^{-1}, for Liquid Methanol

	T/K									
P/bar	298.15	313.15	333.15	353.15	373.15	393.15	413.15	433.15	453.15	473.15
1	1.204	1.254	1.332							
5	1.200	1.249	1.327	1.437	1.600					
10	1.196	1.244	1.321	1.429	1.589	1.826				
25	1.182	1.229	1.302	1.406	1.556	1.778	2.117	2.676		
50	1.161	1.205	1.273	1.369	1.507	1.707	2.004	2.470	3.293	5.138
100	1.121	1.160	1.221	1.304	1.422	1.589	1.826	2.173	2.711	3.627
200	1.053	1.086	1.134	1.200	1.292	1.416	1.584	1.811	2.122	2.560
300	0.998	1.026	1.066	1.120	1.194	1.293	1.422	1.590	1.807	2.089
400	0.951	0.976	1.010	1.056	1.118	1.200	1.304	1.436	1.602	1.808
500	0.911	0.934	0.964	1.003	1.056	1.126	1.213	1.322	1.454	1.616
600	0.877	0.897	0.924	0.958	1.004	1.064	1.139	1.231	1.342	1.474
700	0.847	0.865	0.889	0.919	0.960	1.013	1.078	1.157	1.252	1.363
800	0.820	0.837	0.858	0.885	0.922	0.968	1.026	1.096	1.177	1.273
900	0.796	0.811	0.831	0.855	0.888	0.929	0.981	1.043	1.115	1.198
1000	0.774	0.788	0.806	0.828	0.857	0.895	0.941	0.996	1.061	1.135

Table VI. Thermal Pressure Coefficient, $\gamma_V \equiv (\partial P/\partial T)_V$ bar/K, for Liquid Methanol

	T/K									
P/bar	298.15	313.15	333.15	353.15	373.15	393.15	413.15	433.15	453.15	473.15
1	10.065	9.311	8.422							
5	10.074	9.322	8.437	7.710	7.105					
10	10.085	9.337	8.456	7.733	7.132	6.594				
25	10.118	9.381	8.513	7.801	7.210	6.685	6.166	5.586		
50	10.176	9.457	8.608	7.914	7.340	6.834	6.340	5.801	5.142	4.229
100	10.299	9.615	8.803	8.138	7.593	7.120	6.667	6.189	5.634	4.939
200	10.575	9.949	9.196	8.580	8.079	7.651	7.255	6.853	6.413	5.904
300	10.878	10.299	9.592	9.010	8.538	8.140	7.779	7.422	7.043	6.621
400	11.200	10.657	9.984	9.426	8.974	8.595	8.255	7.925	7.584	7.213
500	11.534	11.019	10.371	9.829	9.388	9.020	8.693	8.381	8.062	7.723
600	11.875	11.383	10.751	10.218	9.783	9.420	9.100	8.798	8.494	8.176
700	12.220	11.742	11.121	10.593	10.159	9.797	9.480	9.184	8.889	8.584
800	12.565	12.098	11.482	10.954	10.519	10.155	9.837	9.543	9.254	8.957
900	12.909	12.449	11.834	11.302	10.862	10.495	10.174	9.879	9.592	9.301
1000	13.250	12.792	12.176	11.638	11.191	10.818	10.493	10.195	9.909	9.620

Table VII. Enthalpy (J/mol) of Liquid Methanol Relative to the Perfect Crystal at 0 K

	T/K									
P/bar	298.15	313.15	333.15	353.15	373.15	393.15	413.15	433.15	453.15	473.15
1	19 276	20 499	22 164							
5	19 286	20 510	22 174	23 892	25 680					
10	19 299	20 522	22 186	23 902	25 689	27 788				
25	19 338	20 560	22 222	23 935	25 717	27 809	29 702	31 845		
50	19 404	20 624	22 282	23 990	25 765	27 845	29 719	31 831	34 678	38 140
100	19 538	20 753	22 405	24 105	25 865	27 926	29 769	31 831	34 587	37 856
200	19 808	21 018	22 659	24 343	26 082	28 111	29 909	31 900	34 547	37 631
300	20 084	21 287	22 920	24 592	26 314	28 319	30 082	32 026	34 603	37 586
400	20 363	21 561	23 186	24 848	26 556	28 541	30 278	32 185	34 713	37 627
500	20 644	21 838	23 456	25 110	26 805	28 774	30 489	32 367	34 856	37 719
600	20 928	22 118	23 730	25 376	27 061	29 016	30 712	32 566	35 024	37 846
700	21 213	22 399	24 006	25 645	27 321	29 264	30 945	32 778	35 210	37 999
800	21 499	22 683	24 285	25 918	27 586	29 518	31 184	33 000	35 409	38 170
900	21 787	22 967	24 565	26 192	27 853	29 775	31 430	33 230	35 620	38 356
1000	22 075	23 252	24 846	26 469	28 123	30 037	31 680	33 466	35 839	38 554

Table VIII. Entropy (J/mol) of Liquid Methanol Relative to the Perfect Crystal at 0 K

	T/K									
P/bar	298.15	313.15	333.15	353.15	373.15	393.15	413.15	433.15	453.15	473.15
1	128.08	132.08	137.24							
5	128.06	132.06	137.21	142.22	147.14					
10	128.04	132.04	137.19	142.19	147.10	152.55				
25	127.96	131.96	137.10	142.09	146.99	152.43	157.10	162.10		
50	127.84	131.84	136.97	141.94	146.82	152.23	156.85	161.78	168.17	175.89
100	127.61	131.59	136.70	141.66	146.50	151.85	156.39	161.21	167.39	174.69
200	127.18	131.14	136.21	141.12	145.90	151.18	155.61	160.26	166.19	173.10
300	126.77	130.71	135.76	140.63	145.37	150.58	154.92	159.46	165.24	171.92
400	126.39	130.31	135.34	140.18	144.88	150.04	154.31	158.77	164.43	170.97
500	126.03	129.93	134.94	139.76	144.42	149.54	153.76	158.14	163.72	170.15
600	125.68	129.58	134.57	139.36	144.00	149.07	153.25	157.58	163.09	169.43
700	125.35	129.23	134.21	138.98	143.59	148.64	152.78	157.06	162.51	168.77
800	125.03	128.91	133.86	138.62	143.21	148.23	152.33	156.57	161.97	168.17
900	124.73	128.59	133.54	138.28	142.84	147.84	151.91	156.11	161.47	167.62
1000	124.43	128.29	133.22	137.95	142.49	147.47	151.51	155.68	161.00	167.10

Derived Properties

We report here the results of detailed calculations of thermodynamic properties of liquid methanol, with only brief accounts of the method used; more complete details can be found in the thesis of Machado (*12*). We have used a value of 32.042 for the molecular weight of methanol and 82.05 cm^3 atm/(mol K) for the gas constant.

Mechanical Coefficients. The mechanical coefficients of liquid methanol, the isothermal compressibility $\beta_T \equiv (-1/V)\cdot(\partial V/\partial P)_T$, the thermal expansion coefficient $\alpha_P \equiv (1/V)(\partial V/\partial T)_P$, and the thermal pressure coefficient $\gamma_V \equiv (\partial P/\partial T)_V$ have been calculated from eq 1 and are recorded in Tables IV–VI. Graphs of these properties show them to be smooth functions of pressure and temperature (*12*).

Enthalpy and Entropy. Enthalpies and entropies for liquid methanol, relative to the perfect crystal at 0 K, are recorded in Tables VII and VIII. To obtain the enthalpies and entropies for the saturated liquid—the low-pressure boundary of our equation of state—we used the method and the data reported by Zubarev et al. (*10*) for the gaseous region and for the vapor pressure curve. Enthalpies and entropies of vaporization were calculated from the Clapeyron equation. In the compressed liquid region changes in enthalpy and entropy with pressure were calculated from standard thermodynamic relations. The values recorded in Tables VII and VIII agree with the data of Zubarev et al. (*10*) to within about 0.1%.

Constant-Pressure Heat Capacity. Changes in heat capacity with pressure can be calculated by using eq 1; however, these calculations involve a second derivative of the *PVT* surface $(\partial^2 P/\partial T^2)$, which can be accurately determined only from *PVT* data of very high precision. We consider the data reported

Table IX. Constant-Pressure Heat Capacity (J/(mol K)) of Liquid Methanol

	T/K									
P/bar	298.15	313.15	333.15	353.15	373.15	393.15	413.15	433.15	453.15	473.15
1	81.18	84.36	89.50							
5	81.16	84.34	89.46	95.86	103.94					
10	81.13	84.30	89.42	95.79	103.84	114.23				
25	81.05	84.21	89.29	95.60	103.54	113.76	127.36	146.55		
50	80.92	84.06	89.09	95.30	103.08	113.04	126.17	144.38	171.84	221.12
100	80.67	83.79	88.72	94.76	102.28	111.81	124.25	141.13	165.62	206.30
200	80.23	83.32	88.09	93.86	100.98	109.93	121.45	136.84	158.67	194.18
300	79.86	82.93	87.58	93.15	99.96	108.50	119.44	133.98	154.53	188.02
400	79.52	82.59	87.15	92.55	99.13	107.36	117.89	131.87	151.62	183.99
500	79.22	82.29	86.78	92.03	98.43	106.41	116.63	130.20	149.40	181.04
600	78.95	82.03	86.45	91.59	97.83	105.61	115.58	128.83	147.62	178.73
700	78.70	81.79	86.16	91.20	97.30	104.91	114.68	127.67	146.15	176.86
800	78.47	81.57	85.89	90.85	96.83	104.30	113.89	126.68	144.89	175.29
900	78.25	81.37	85.66	90.53	96.42	103.76	113.20	125.81	143.81	173.95
1000	78.06	81.19	85.44	90.25	96.04	103.27	112.58	125.04	142.86	172.79

Table X. Properties of Liquid and Gaseous Methanol at Saturation[a]

T/K	P/bar	V^G/ (cm^3/g)	V^L/ (cm^3/g)	H^G/ (J/mol)	ΔH^{vap}/ (J/mol)	S^G/ (J/(mol K))	$10^3\beta_T$/ bar^{-1}	$10^3\alpha_P$/ K^{-1}	γ_V/ (bar/K)
298.15	0.169	4484.6	1.2711	56 768.8	37 495.1	253.8	0.120	1.205	10.063
313.15	0.353	2232.1	1.2947	57 226.1	36 728.3	249.4	0.135	1.255	9.308
323.15	0.553	1457.0	1.3112	57 496.5	36 170.4	246.6	0.146	1.291	8.843
333.15	0.841	977.3	1.3285	57 737.0	35 572.9	244.0	0.158	1.334	8.418
343.15	1.246	671.9	1.3465	57 947.2	34 934.9	241.5	0.172	1.384	8.035
353.15	1.801	472.2	1.3656	58 126.5	34 241.9	239.2	0.188	1.446	7.688
363.15	2.546	338.7	1.3857	58 278.9	33 510.5	237.0	0.206	1.520	7.371
373.15	3.524	247.5	1.4071	58 406.6	32 729.5	234.9	0.228	1.611	7.079
383.15	4.790	183.8	1.4302	58 511.8	31 871.1	232.9	0.253	1.723	6.801
393.15	6.387	138.8	1.4551	58 603.4	30 819.8	231.0	0.285	1.860	6.532
403.15	8.376	106.3	1.4824	58 682.4	29 910.9	229.3	0.325	2.032	6.532
413.15	10.834	82.2	1.5124	58 741.9	29 047.9	227.6	0.376	2.252	5.983
423.15	13.843	64.0	1.5459	58 771.7	28 081.1	226.0	0.447	2.543	5.684
433.15	17.490	50.1	1.5837	58 759.3	26 907.5	224.5	0.551	2.947	5.353
443.15	21.855	39.4	1.6272	58 686.1	25 477.1	222.9	0.714	3.551	4.970
453.15	27.024	30.9	1.6780	58 524.4	23 775.1	221.2	1.017	4.578	4.503
463.15	33.083	24.2	1.7391	58 229.5	21 792.6	219.4	1.783	6.902	3.871
473.15	40.137	18.8	1.8146	57 730.4	19 501.0	217.3			2.521

[a] The superscripts G and L refer to saturated gas and liquid, respectively; ΔH^{vap} is the enthalpy of vaporization, β_T is the isothermal compressibility, and α_P is the thermal expansion coefficient. The saturated-gas volumes, V^G, entropies, S^G, and enthalpies, H^G, are from Zubarev et al. (*10*).

here to be of marginal precision for this use. Nevertheless, we have calculated constant-pressure heat capacities of the compressed liquid from eq 1, using published data for the heat capacity of the saturated liquid up to 325 K (*14*, *15*) and a simple extrapolation beyond that temperature. The calculated heat capacities are recorded in Table IX; error in these values may well exceed 20% at high temperatures and pressures.

Saturated Gas and Liquid. Properties of saturated liquid and gaseous methanol, calculated from eq 1 and the data of Zubarev et al. (*10*), are recorded in Table X. For the sake of completeness we have included volumes, entropies, and enthalpies of the saturated gas, taken entirely from Zubarev et al.

Conclusions

The direct-weighing method of *PVT* measurements is simple and straightforward and can lead to results of high accuracy with modest investments of time and equipment. It is particularly well suited for measurements at high pressures and moderately high temperatures.

We have calculated tables of thermodynamic properties for liquid methanol within a limited range of pressures and temperatures. Further measurements are needed, especially in the critical region, before more complete tables of thermodynamic properties can be constructed.

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