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PVT Properties of Methanol at Temperatures to 300°C

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Measurements of the PVT behavior of compressed gas and liquid methanol are reported. Pressure versus temperature observations were made along paths of very nearly constant density (pseudoisochores) in the temperature range from about 100 to 300°C and at pressures to about 35 MPa. Eighteen pseudoisochores were determined, ranging in density from about 2 to 22 $\mathrm{mol \cdot dm^{-3}}$.

KEY WORDS: compressed gas; compressed liquid; compressibility; density; fluids; measurements; methanol; PVT behavior.

1. INTRODUCTION

Although PVT data for methanol at elevated temperatures are available from a number of sources [1–5], the data are fragmented and often inconsistent. Accurate broad-range data are necessary for engineering calculations, derivation of thermodynamic quantities, and equation-of-state development [6]. Only the data of Machado and Street [1] on the compressed liquid at temperatures below about 215°C and those of Zubarev and Bagdonas [3] at temperatures to 300°C appear to be sufficient accuracy for these purposes.

We report measurements of the PVT behavior of compressed methanol in the temperature range from about 100 to 300°C at pressures to about 35 MPa. Pressure versus temperature observations were made along paths of very nearly constant density (pseudoisochores). Eighteen pseudoisochores were determined, ranging in density from about 2 to 22 $\mathrm{mol \cdot dm^{-3}}$.

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2. EXPERIMENT

Measurements were made using a recently constructed automated high-temperature PVT apparatus which has been described in detail elsewhere [7]. The apparatus is shown schematically in Fig. 1. The 120-cm^3 spherical cell, valves, and piping were constructed of 316 stainless steel. A large thermal mass in the form of an aluminium block surrounds, but is not in contact with, the cell to minimize thermal gradients and fluctuations inherent in the stirred air oven used as the thermostat. A very low-power shimming heater located in the air stream above the cell provides precise temperature control to the cell.

Cell temperatures are calculated from the temperature of the block, as determined by the primary thermometer, and the small temperature differences between the block and the cell as determined by appropriately placed differential thermocouples. The primary thermometer is a platinum

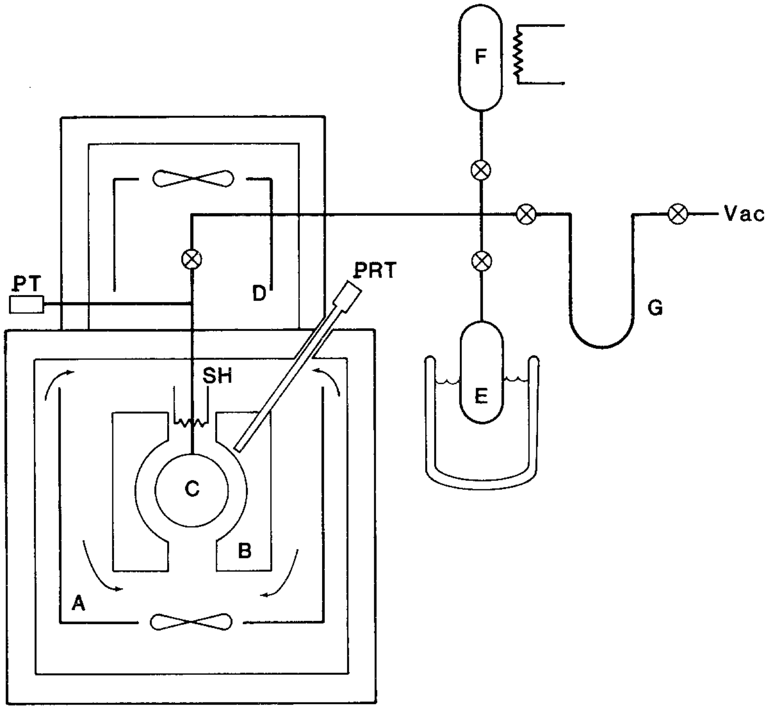

Fig. 1. Schematic of experiental apparatus. A, Main thermostat; B, aluminium block; C, cell; D, upper thermostat; PT, pressure transducer; PRT, platinum resistance thermometer; E, condensing cell; F, storage and filling cell; G, vapor trap (see also Ref. 7).

resistance thermometer calibrated with respect to the IPTS 1968 by the National Bureau of Standards.

Pressures were determined from the frequency of a commercial vibrating quartz pressure transducer calibrated against the primary deadweight gauge and are estimated to be accurate to the greater of 5 kPa or 0.05 %.

Methanol samples were 99.9 % pure high-purity liquid chromatographic grade which were stored over activated Al_2O_3 for removal of water. Samples were distilled from the storage vessel into a second portable cylinder for injection into the apparatus. Gas chromatographic analysis of the methanol samples prior to filling indicated a maximum water content of less than 0.01 % and an organic content less than our detectable limit of 1 ppm.

The cell is filled by heating the methanol cylinder to a temperature slightly above that of the evacuated cell and manipulating the appropriate valves. After filling to near the desired starting density, the pressure versus temperature data are accumulated automatically under the control of a small desk-top computer. The cell temperature is brought to within 0.1 °C of the preprogrammed target temperature, after which the computer continuously refines the temperature to within a few hundredths of a degree of the target temperature. After an equilibration period (usually 1 h) the data are logged by the computer, but only if the temperature difference from the target temperature and temperature and pressure drift rates are within specified preprogrammed limits. The process is repeated under computer control until the preset maximums in temperature or pressure are reached. A typical experimental "run" took from 17 to 35 h depending on the density.

At the completion of a run, the methanol is then condensed from the system into a detachable cylinder held at liquid nitrogen temperature for subsequent weighing. Densities assigned to each point are calculated from the mass of the methanol and the calibrated volume of the system. Small corrections are made for thermal expansion and pressure dilation of the cell and for the small quantities of methanol residing in the various noxious volumes.

3. RESULTS AND DISCUSSION

At temperatures above approximately 240°C thermal degradation of the methanol produced an observable rise in the measured pressure with time for replicate measurements. The equivalent error in terms of the density, however, was always less than 0.1 %, even if uncorrected.

Evidence has been found which indicates that the rate of thermal degradation of the methanol samples is affected by the containing material and that 316 SS tends to catalyze the decomposition of methanol [8]. Such phenomena would tend to make the results of any PVT measurement on methanol somewhat dependent on the experimental apparatus used to obtain the data and on the residence time of the methanol in the apparatus.

An attempt has been made to adjust the higher-temperature data for apparatus effects to make the data more independent of the apparatus. Since the computer recorded not only the experimental parameters, but also the time at various temperatures, a nearly complete thermal history of the samples is available. A series of pressure observations at fixed temperatures of 250, 275, and 300°C, lasting for over 50 h each, was made for seven different but fixed densities from which the rate of change of pressure with time could be obtained. The data are shown in Fig. 2. From these data an approximate surface describing the rate of change of pressure in the form

$$\left(\frac{\partial P}{\partial t}\right)_\rho = \beta(T)\,\rho \tag{1}$$

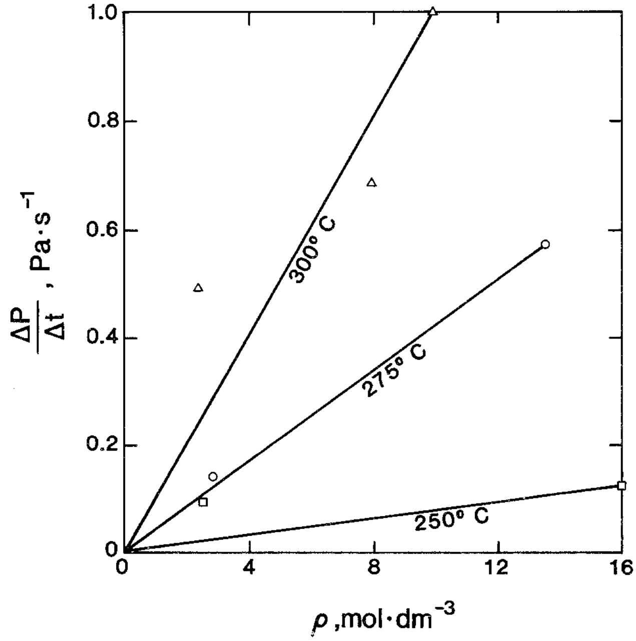

Fig. 2. Change in the measured pressure versus time at selected densities and temperatures. △, 300°C; ○, 275°C; □, 250°C.

Table I. PVT Data for Methanol

Density ($mol \cdot dm^{-3}$)	Temperature (°C)	Pressure (MPa)
2.061	209.977	4.762
2.061	215.008	4.961
2.060	220.004	5.159
2.059	225.007	5.373
2.059	230.046	5.558
2.058	235.054	5.734
2.057	240.056	5.904
2.057	244.935	6.067
2.056	250.028	6.225
2.055	255.010	6.384
2.055	260.007	6.528
2.054	269.980	6.819
2.052	280.058	7.101
2.051	290.046	7.374
2.050	300.025	7.641
2.112	214.983	5.008
2.111	220.008	5.202
2.110	225.019	5.401
2.110	229.902	5.605
2.109	234.908	5.789
2.108	239.932	5.966
2.108	244.903	6.136
2.107	250.026	6.303
2.107	254.986	6.465
2.106	259.976	6.618
2.105	269.961	6.919
2.103	280.012	7.216
2.102	290.060	7.503
2.101	299.979	7.777
2.691	219.972	5.689
2.690	225.029	5.946
2.689	229.977	6.198
2.688	235.015	6.438
2.687	240.029	6.695
2.687	245.054	6.937
2.686	249.990	7.164
2.685	255.046	7.383
2.684	260.055	7.595
2.683	270.058	8.013
2.681	280.057	8.414
2.679	289.917	8.796
2.678	300.021	9.174
3.232	229.966	6.597
3.231	234.965	6.895

Table I. *(Continued)*

Density (mol · dm^{-3})	Temperature (°C)	Pressure (MPa)
3.230	240.041	7.209
3.229	244.957	7.505
3.228	249.989	7.788
3.227	254.987	8.064
3.227	259.951	8.335
3.225	269.960	8.863
3.223	280.003	9.370
3.221	290.056	9.862
3.219	300.034	10.337
3.888	234.994	7.257
3.887	240.026	7.636
3.886	245.005	7.998
3.885	250.000	8.350
3.884	255.037	8.699
3.883	259.977	9.035
3.880	269.993	9.698
3.878	280.001	10.337
3.876	290.015	10.957
3.873	299.982	11.559
4.586	235.012	7.460
4.584	240.053	7.901
4.583	244.997	8.328
4.581	250.036	8.750
4.580	254.924	9.158
4.579	260.029	9.570
4.576	269.967	10.364
4.573	280.030	11.142
4.570	289.974	11.894
4.568	299.937	12.629
5.349	240.027	8.067
5.347	244.975	8.565
5.345	249.983	9.056
5.344	254.999	9.541
5.342	259.979	10.019
5.339	270.019	10.964
5.336	280.041	11.887
5.333	290.041	12.790
5.329	300.035	13.673
6.713	239.961	8.164
6.711	244.985	8.770
6.709	249.981	9.367
6.707	254.986	9.965
6.705	259.977	10.559
6.701	269.977	11.745

Table I. *(Continued)*

Density $(mol \cdot dm^{-3})$	Temperature (°C)	Pressure (MPa)
6.697	280.031	12.924
6.693	290.041	14.089
6.689	300.011	15.240
6.756	240.039	8.173
6.754	245.047	8.780
6.752	250.046	9.380
6.750	255.037	9.980
6.748	260.031	10.579
6.744	269.977	11.766
6.740	279.959	12.948
6.736	289.974	14.123
6.732	299.962	15.285
8.370	239.967	8.188
8.367	245.011	8.892
8.365	250.037	9.606
8.362	254.998	10.324
8.360	259.984	11.050
8.355	269.963	12.520
8.350	279.973	14.002
8.345	290.068	15.496
8.340	300.037	16.978
9.779	239.979	8.195
9.776	245.015	8.990
9.773	250.028	9.813
9.770	254.984	10.650
9.767	260.043	11.512
9.761	270.036	13.256
9.755	280.061	15.033
9.750	290.068	16.827
9.744	300.027	18.629
11.077	239.987	8.274
11.070	250.018	10.152
11.063	259.979	12.132
11.050	280.029	16.288
11.037	300.014	20.576
12.382	239.944	8.563
12.379	244.954	9.670
12.375	250.026	10.817
12.371	255.034	11.987
12.367	260.022	13.176
12.360	269.949	15.603
12.352	279.993	18.104
12.345	290.048	20.646
12.337	300.050	23.211

Table I. *(Continued)*

Density (mol·dm^{-3})	Temperature (°C)	Pressure (MPa)
13.417	235.016	7.977
13.413	240.027	9.238
13.408	244.980	10.530
13.404	250.018	11.863
13.400	254.958	13.209
13.396	259.977	14.593
13.388	270.012	17.419
13.380	279.961	20.288
13.371	289.967	23.216
13.363	299.966	26.177
14.764	224.972	6.647
14.759	229.971	8.141
14.754	234.959	9.671
14.750	239.969	11.246
14.745	244.960	12.849
14.740	249.971	14.483
14.736	255.025	16.150
14.731	260.043	17.833
14.722	269.957	21.235
14.713	279.959	24.709
14.704	290.055	28.250
14.695	299.971	31.799
16.113	214.967	6.105
16.107	219.962	7.902
16.102	225.019	9.754
16.097	229.973	11.630
16.091	235.039	13.554
16.086	240.028	15.501
16.081	244.952	17.463
16.076	249.969	19.465
16.071	254.936	21.481
16.066	260.060	23.553
16.056	269.956	27.670
16.046	280.053	31.883
17.022	204.990	5.593
17.016	210.016	7.629
17.010	214.996	9.704
17.004	220.006	11.827
16.999	224.966	13.980
16.993	229.954	16.171
16.988	235.020	18.405
16.982	240.023	20.494
16.977	244.972	22.714
16.972	249.957	24.982

Table I. *(Continued)*

Density (mol·dm^{-3})	Temperature (°C)	Pressure (MPa)
16.966	254.965	27.278
16.961	259.965	29.576
16.956	264.968	31.907
16.956	265.027	31.922
18.884	174.988	2.543
18.821	180.014	4.604
18.814	184.987	7.079
18.808	190.018	9.620
18.801	195.020	12.209
18.795	199.969	14.829
18.789	204.944	17.489
18.782	210.029	20.215
18.776	215.019	22.949
18.770	219.961	25.709
18.764	224.980	28.518
18.758	229.962	31.345
18.752	235.015	34.210
19.263	170.031	2.848
19.199	175.018	4.995
19.192	179.981	7.567
19.185	185.025	10.230
19.179	190.003	12.906
19.172	195.032	15.656
19.166	200.034	18.432
19.160	205.027	21.237
19.153	210.026	24.092
19.147	214.971	26.966
19.141	219.954	29.859
19.135	225.030	32.816
20.108	159.962	6.308
20.094	169.982	12.085
20.080	179.966	18.044
20.066	190.007	24.193
20.053	199.984	30.484
22.116	105.014	2.633
22.052	109.968	5.124
22.043	115.014	8.480
22.035	119.972	11.867
22.027	124.992	15.301
22.020	129.994	18.794
22.012	135.009	22.333
22.005	139.983	25.905
21.998	145.000	29.539
21.990	149.984	33.199

was fit. In Eq. (1) P, ρ, T, and t are the pressure, density, temperature, and time, respectively, and

$$\beta(T) = a_0 + a_1\left(\frac{T}{T_0}\right) + a_2\left(\frac{T}{T_0}\right)^2 \tag{2}$$

where T_0 is a convenient reducing temperature and the a_i's are fitting parameters. It was found that the approach to thermal equilibrium could be closely approximated in the form,

$$T(t) = T_2 - \Delta T e^{-\alpha \Delta t} \tag{3}$$

where $\Delta T = T_2 - T_1$, T_i is the temperature of data point i, and Δt is the time interval between points. Sufficient data were recorded to obtain the

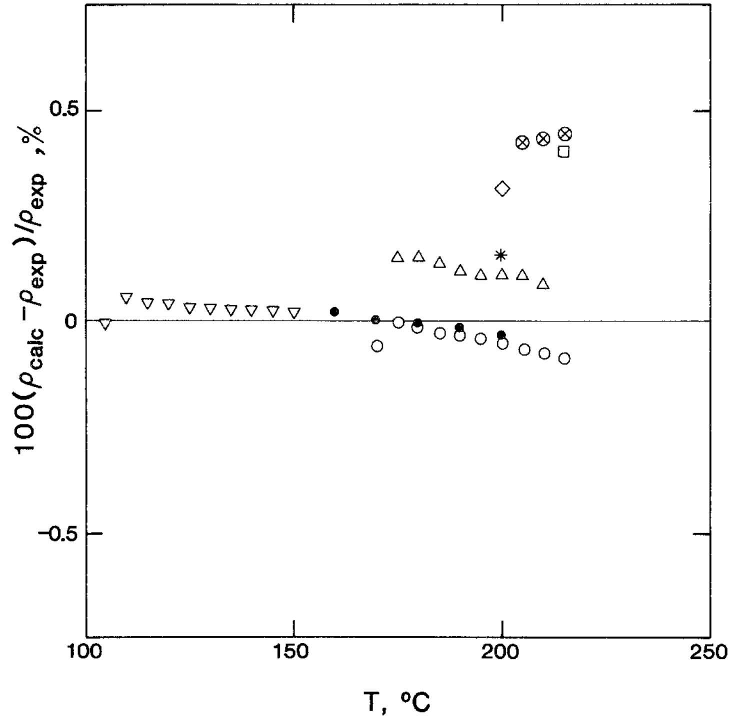

Fig. 3. Comparison of our density data primarily with the data of Ref. 1. Density deviations are plotted relative to the equation of state of Ref. 1. Some points from Ref. 3 are also shown: (▽, ●, ○, △, ⊗, □) nominal densities of 22.1, 20.1, 19.2, 18.8, 17.0, and 16.1 mol · dm^{-3}, respectively. (*, ◇) data of Ref. 3 at nominal densities of 19 and 17 mol · dm^{-3}, respectively.

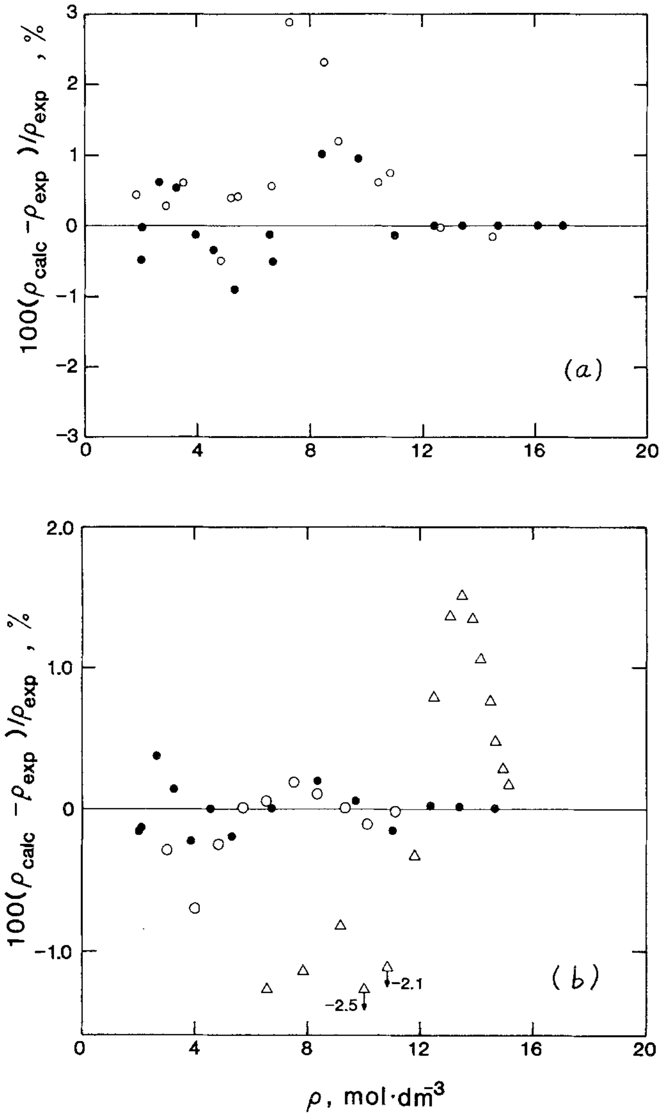

Fig. 4. Comparison of our densities with densities of Ref. 3 at 250°C (a) and 300°C (b). Deviations are relative to a polynomial fit to the data of this work. Absolute deviations from the baseline reflect only the ability of the polynomial to fit the data. ●, this work; ○, Ref. 3; △, Ref. 5.

value of α for each heating interval. Using Eqs. (1), (2), and (3) a pressure correction, $\Delta\rho_{ij}$, for all data points could be computed with

$$\Delta P_{ij} = -\rho \int_{t_i}^{t_i + \Delta t_{ij}} \beta(T)\, dt \tag{4}$$

where $\Delta t_{ij} = t_j - t_i$ is the heating time interval from point i to point j. This correction increases with both temperature and density. However, since density decreases with temperature, the effect reaches a maximum at intermediate densities near the critical region at temperatures above 240°C. Although the net effect on the pressure (or the equivalent density) is small, the isochore curvatures could be expected to be altered somewhat, affecting thermodynamic calculations in this region.

The corrected data, tabulated in Table I, are generally in good agreement with both Ref. 1 and Ref. 3 in the region of overlap. The data are compared to the data of Ref. 1 in Fig. 3. For this comparison we use the equation of state of Ref. 1 to compare densities at slightly different pressures and temperatures without multiple interpolation. Excellent agreement is found at the lower temperatures and higher densities. However, deviations of a few tenths of a percent exist at the higher temperature and lower density extremes of Ref. 1. Figures 4a and b illustrate a comparison primarily with data of Ref. 3 at selected temperatures. These deviations are plotted relative to a polynomial fit to the 250 or 300°C isotherms obtained from our work. Absolute deviations from the baseline indicate only the ability of the polynomial to reproduce the experimental points. However, good agreement with the data of Ref. 3 is indicated by the fact that both the data sets exhibit similar trends and fall within a narrow band of about 0.2%, except at the lowest densities and in the critical region, where the data would be expected to exhibit more scatter. The differences between Ref. 5 and this work, also shown in Fig. 4b, are considerably larger, reaching as much as 2.5%, well outside our experimental uncertainty, estimated at ±0.2% in density.

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REFERENCES

1. J. R. S. Machado and W. B. Street, *J. Chem. Eng. Data* **28**:218 (1983).
2. R. Ta'ani, Ph. D. thesis (Universität Karlsruhe, Karlsruhe, West Germany, 1976).
3. V. N. Zubavev and A. V. Bagdonas, *Therm. Eng.* (English transl.) **14**:111 (1967).
4. L. M. Lashokov, *Acta Physicochim. USSR* **11**:108 (1939).
5. R. S. Finkelstein and L. I. Stiel, *Chem. Eng. Prog. Symp. Ser.* **66**:11 (1970).
6. R. D. Goodwin, Unpublished data.
7. G. C. Straty and A. M. F. Palavra, *J. Res. Natl. Bur. Stand.* **89**(5):375 (1985).
8. For a more extensive and quantitative discussion of the behavior of methanol at elevated temperatures and in contact with stainless steel, see T. J. Bruno and G. C. Straty, *J. Res. Natl. Bur. Stand.* **91**(3):135 (1986).