Table III. Coefficients A_i in Eq 1 and Standard Deviations $\sigma(H^E)$, Eq 2, at 298.15 K for Dimethyl Carbonate (1) + Solvents (2)

solvent	A_0	A_1	A_2	A_3	$\sigma(H^E)$/ J mol^{-1}
hexane	7608.9	-375.4	1887.8	-166.7	8
heptane	7953.5	-54.7	1959.1	426.8	9
octane	8210.7	-24.5	2070.2	852.3	10
decane	8818.9	151.4	2269.1	2001.8	10
cyclohexane	7786.9	-203.4	1640.7	-1243.2	9
methylcyclohexane	7449.6	-21.0	1740.5	-698.4	7
benzene	1602.4	200.7	-3.2	-171.5	2
toluene	2046.7	327.4	135.4	-224.5	3
tetrachloromethane	2109.6	-373.4	424.5	-172.2	3

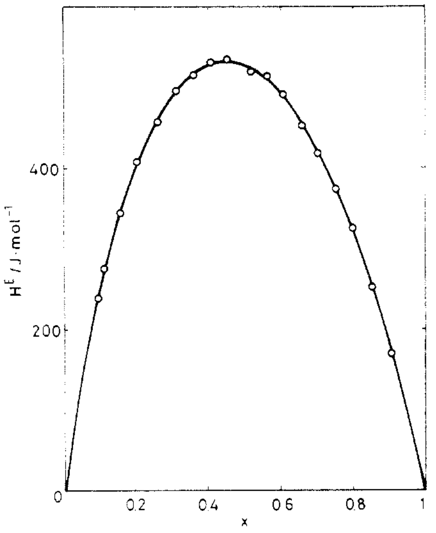

Figure 4. Excess molar enthalpy H^E for dimethyl carbonate (1) + tetrachloromethane (2) mixture versus x_1, the mole fraction of component 1. Full curve represents the smoothing eq 1 with coefficients of Table III.

CH_2-CO-CH_2-CH_3, ca. 1000 J mol^{-1}, and methyl propionate, CH_3-CH_2-CO-O-CH_3, ca. 1200 J mol^{-1} (*14-16*). There is no direct correlation between H^E and the molecular dipole moment: 2.88 D (acetone), 1.72 D (methyl acetate), and 0.90 D (dimethyl carbonate), all the dipole moments for the gas phase (*17*). Obviously each O atom attached to CO, while decreasing the overall electric dipole moment, increases the dissimilarity between the force fields of the polar compounds and the alkane, and hence also H^E.

With nonpolar but strongly polarizable solvents such as benzene and CCl_4 the H^E ($x_1 = 0.5$) values of dimethyl carbonate, methyl acetate, and acetone are ca. 1400-1500 J mol^{-1} smaller, due to the exothermic dipole-induced dipole interaction. For the series with the normal alkane H^E increases as the chain length of the alkane.

A quantitative treatment in terms of DISQUAC, an extended quasi-chemical group contribution method (*2*), of these results and of additional H^E measurements on diethyl carbonate (*18*), will be presented in a forthcoming paper.

Registry No. CH_3-O-CO-O-CH_3, 616-38-6; hexane, 110-54-3; heptane, 142-82-5; octane, 111-65-9; decane, 124-18-5; cyclohexane, 110-82-7; methylcyclohexane, 108-87-2; benzene, 71-43-2; toluene, 108-88-3; tetrachloromethane, 56-23-5.

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Thermodynamic Properties of Methanol from 288 to 503 K and at 8.3 MPa

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Specific heats of methanol have been measured from 393 to 503 K and at 8.3 MPa, using a high-temperature and high-pressure flow heat capacity calorimeter. These data have been supplemented with specific heats at lower temperatures, taken from the literature and corrected to 8.3 MPa, to obtain a consistent set of molar heat capacities from 288 to 503 K. The heat capacities have been fitted to a four-parameter equation and the equation has been employed to evaluate $H_T - H_{298}$ and $S_T - S_{298}$ for methanol from 298 to 503 K at 8.3 MPa.

Introduction

Methanol is a major solvent in the chemical industry, and energy crises of the past several years have increased its importance as a fuel additive and as a potential solvent in absorption type refrigerators and air conditioners. Notwithstanding this increased interest, the thermodynamic properties of methanol, especially at elevated temperatures and pressures, are sparse. Precise heat capacities of the saturated liquid have been measured from low temperatures to 325 K by Carlson (*1*), from 323 to 353 K by Hough, Mason, and Sage (*2*), and at 298

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K by Benson, D'Arcy, and Kiyohara (3). Fiock, Ginnings, and Holton (4) have reported heat capacities from 313 to 373 K, calculated from enthalpy measurements. Wilhoit, Chao, and Hall (5) have critically examined heat capacity data and have assigned a standard state value at 298.15 K, and Touloukian and Makita (6) have examined many heat capacity data for the liquid state up to 383 K. Machado and Streett (7) have published heat capacities at temperatures up to 473 and at high pressures, derived from an extrapolation of the saturated heat capacities of Carlson's from 325 K, and corrected to higher pressures by an equation of state. Since pressure corrections to the heat capacity require second derivatives of the volume with respect to temperature, such corrections are subject to considerable error. Machado and Streett state that the error in their published heat capacities may exceed 20% at higher temperatures and pressures. Yerlett and Wormald (8) have reported directly measured relative specific enthalpies of methanol from 373.2 to 573.2 K, and from 0.1 to 13.6 MPa. They report an overall accuracy of 0.6%. However, their values are generally more than 5% higher than the relative enthalpies reported by Machado and Streett, after the data have been corrected to 8.3 MPa. Data reported in the latter work are internally inconsistent. The enthalpies reported by Machado and Streett are based on a different literature source than their reported heat capacities. Recently, Goodwin (9) has calculated various thermal properties for methanol up to 673 K and 70 MPa from vapor pressure and density data.

In connection with another study, it was necessary for us to obtain reliable values for the heat capacity of pure anhydrous methanol to temperatures approaching the critical temperature. The purpose of this paper is to report the results of these measurements, to use the data to calculate a consistent set of relative enthalpies and entropies at 8.3 MPa, and to critically examine the reliability of previous measurements.

Experimental Section

Details of construction of the calorimeter are reported elsewhere (10). For this study the stainless steel capillary tubing was replaced with Hastalloy-C tubing and the resistances of the thermistors were increased so that the calorimeter would operate at higher temperatures. In addition, the calorimeter was placed in a high-temperature air bath, controlled to ±0.002 K. Because of the poor heat transfer from air to the capillary tubing leading to and from the calorimeter, a pre and post heat sink was installed to maintain the temperature of the capillaries entering and leaving the bath to within about 0.1 K of the bath temperature. This heat sink was made from a 1 ft length of a 6 in. diameter solid aluminum cylinder, grooved so that the 1.5 m long $^1/_{16}$-in. capillaries would make good thermal contact with the cylinder. The temperature of the cylinder was controlled to 0.01 K. The capillary system was pressurized by an ISCO Model LC5000 high-pressure syringe pump and a Circle Seal BPR21 back-pressure regulator. Sample introduction was accomplished with a series of high-pressure switching valves, using the same techniques as in the previous measurements (10).

The specific heat of methanol, on a per volume basis, is close to that of water in the 393–503 K temperature range. This allowed pure water to be employed as the reference fluid, so that the specific heat of methanol was measured relative to the known specific heat of water (11). The heat loss factors (f factors) for both liquids were determined by the delta-flow method (12). A second high-pressure syringe pump (ISCO Model 314) was employed to introduce additional small quantities of fluid into the capillary system during the f-factor determination. The overall performance of the calorimeter at each temperature was evaluated by measuring the specific heats of a series of aqueous NaCl solutions. The values for the salt solutions matched the literature values (13) within 0.1% at every temperature and concentration; the average difference was less than 0.04%.

All measurements were performed at 8.3 MPa; the critical pressure of methanol is 8.1 MPa. At this pressure and in the range of temperatures investigated, the volume specific heat curves of water and methanol cross. Throughout this study the fluid passing through the reference side of the calorimeter was always that fluid with the greatest per volume specific heat at the given temperature. Because of this, the "reference" fluid and the "measured" fluid interchanged, depending upon the temperature.

Methanol (Fisher ACS Certified) used in the measurements was prepared by drying over 3A molecular sieves for 24 h, followed by 24 h over calcium hydride chips, and finally distilling from calcium hydride. Yerlett and Wormald (8) have examined the extent of decomposition of methanol at high temperatures and have concluded that decomposition is negligible at temperatures below 498.2 K. Since our measurements extend only to 503 K, and the methanol is at this high temperature only for the brief period that it is flowing through the calorimeter, very little impurity is introduced from decomposition. All water was house distilled water which had been further purified by passing through an activated charcoal filter and ion-exchange column, followed by boiling for deaeration.

Results and Discussion

The general equation for determining the specific heat on a mass basis of a fluid (2) from the known specific heat of a reference fluid (1) is (14)

$$c_{p,2} = c_{p,1}[d_1/d_2]\{1 - [(f_2P_2 - f_1P_1)/P_1]\} \qquad (1)$$

where f is the heat loss factor, d is the density at the working pressure, and P is the power input to the calorimeter for fluids 1 and 2. It has been shown (15) that one needs only to know the relative densities of the fluids at one fixed temperature. The density ratio for water and methanol at 298 K and 8.3 MPa used in these calculations was 1.259 01. The specific heats calculated from this equation at 393 K and above have been converted to molar heat capacities and are listed in the second column of Table I. Uncertainties associated with these values are our best estimate of the errors at each temperature. The low uncertainty at 473.15 K is a reflection of the close values of the volume specific heats for water and methanol at this temperature. The calorimeter gives its most accurate values at the point where the volume specific heats of the reference and measured fluids are equal.

Heat capacities from 288 to 373 K, also listed in the second column of Table I, are those reported by Carlson (1), Hough et al. (2), Benson et al. (3), and Fiock et al. (4), which have been corrected to a pressure of 8.3 MPa, using the density data from Machado and Streett (7). The molar heat capacity data covering the entire temperature range from 288 to 503 K have been fitted to a polynomial expression that contains a diverging term to mimic its divergence at the critical point. The expression is

$$C_p = A + BT + CT^2 + D|(T - T_c)/T_c|^{-0.793} \qquad (2)$$

where A, B, C, and D are constants, and T_c is the critical temperature (512.64 K (16)). The critical exponent is that for the divergence of the heat capacity given by Griffiths and Wheeler (17) at the critical point $(1 - 1/\delta)$. The currently accepted value for δ of 4.82 is given by Sengers and Levelt Sengers (18). Values calculated from eq 2, along with their deviations from the experimental points, are included in the third and fourth columns of Table I. The standard deviation of the fit is 2.71 J K^{-1} mol^{-1}. This is lower than one would expect

Table I. Heat Capacities of Anhydrous Methanol at 8.3 MPa

	$C_p/(\mathrm{J\ K^{-1}\ mol^{-1}})$			
temp/K	exptl[e]	eq 2	Δ	ref 7
287.97	79.21 ± 0.32[a]	79.69	−0.48	
297.41	80.85 ± 0.32[a]	80.87	−0.02	
298.15	80.98 ± 0.32[b]	80.98	0.00	80.75
306.81	82.64 ± 0.33[a]	82.37	0.27	
313.15	83.14 ± 0.33[c]	83.55	−0.41	83.89
316.1	84.60 ± 0.34[a]	84.15	0.45	
323.15	85.50 ± 0.34[c]	85.71	−0.21	
323.15	85.66 ± 0.34[d]	85.71	−0.05	
325.17	86.56 ± 0.35[a]	86.19	0.37	
333.15	88.06 ± 0.35[c]	88.23	−0.17	88.85
333.15	88.70 ± 0.36[d]	88.23	0.47	88.85
343.15	90.82 ± 0.36[c]	91.11	−0.29	
343.15	91.91 ± 0.37[d]	91.11	0.80	
353.15	93.76 ± 0.38[c]	94.37	−0.61	94.94
353.15	94.82 ± 0.38[d]	94.37	0.45	94.94
363.15	96.89 ± 0.39[c]	98.01	−1.1	
373.15	100.2 ± 0.40[c]	102.0	−1.8	102.6
393.15	115.0 ± 2.2	111.3	3.7	112.5
433.15	136.3 ± 1.5	135.5	0.84	142.4
473.15	164.2 ± 0.6	171.9	−7.7	212.0
493.15	213.9 ± 1.2	206.1	7.9	
503.15	246.6 ± 2.4	248.9	−2.3	

[a] Carlson (*1*). [b] Benson et al. (*3*). [c] Fiock et al. (*4*). [d] Hough et al. (*2*). [e] All errors for literature values were estimated to be 0.4%.

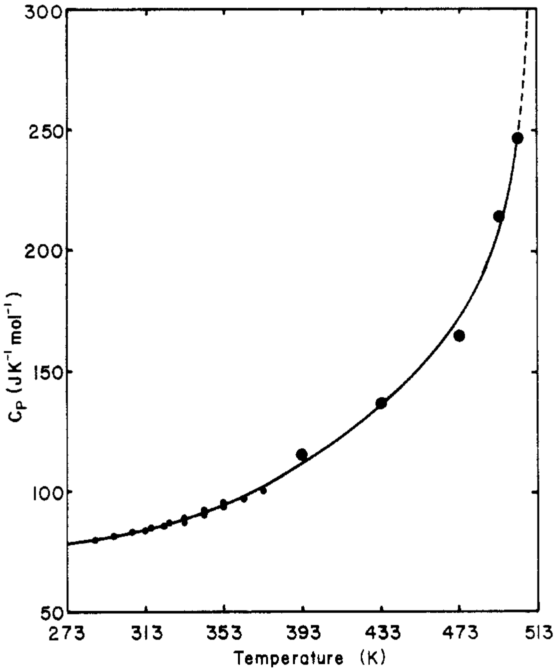

Figure 1. Heat capacity of anhydrous methanol as a function of temperature. The curve is produced by eq 2; the large circles are from this work; the small circles are from the literature.

because of the large number of points at the lower temperatures where the precision of the data is better. Agreement between the experimental values and eq 2 is excellent, considering the few number of parameters used, the wide temperature range covered, and the approach to the critical point. Heat capacities reported by Machado and Streett up to 473.15 K, corrected to 8.3 MPa, are also included in Table I for comparison. Figure 1 shows eq 2 (solid line), along with the various experimental data. The fitting constants for eq 2 are A = 185.84, B = −0.86860, C = 0.0016572, and D = 3.4066. The fourth term in eq 2 is relatively insensitive to the value of the exponent over the temperature range investigated and an arbitrary assignment of −1.0 to this parameter has little effect on calculated thermodynamic functions. While substitution would simplify the integrations discussed below, we have elected to retain the theoretically based value.

Table II. Relative Enthalpies and Entropies of Anhydrous Methanol at 8.3 MPa

	$(H_T - H_{298})/(\mathrm{kJ\ mol^{-1}})$		
temp/K	this work	lit	$(S_T - S_{298})/(\mathrm{J\ K^{-1}\ mol^{-1}})$
298.15	0.0	0.0	0.0
303.15	0.407		1.353
308.15	0.818		2.697
313.15	1.233	1.218[a]	4.034
318.15	1.653		5.366
323.15	2.079		6.693
328.15	2.510		8.018
333.15	2.948	2.873[a]	9.343
338.15	3.393		10.67
343.15	3.845		11.99
348.15	4.304		13.32
353.15	4.772	4.577[a]	14.66
358.15	5.248		16.00
363.15	5.733		17.34
368.15	6.228		18.69
373.15	6.733	6.345[a] 6.786[b]	20.06
378.15	7.249		21.43
383.15	7.775		22.81
388.15	8.314		24.21
393.15	8.864	8.414[a]	25.62
398.15	9.427	9.332[b]	27.04
403.15	10.00		28.48
408.15	10.59		29.93
413.15	11.20	10.27[a]	31.40
418.15	11.82		32.89
423.15	12.45	12.25[b]	34.40
428.15	13.10		35.93
433.15	13.77	12.36[a]	37.49
438.15	14.46		39.06
433.15	15.16		40.66
448.15	15.89	15.36[b]	42.29
453.15	16.63	15.14[a]	43.94
458.15	17.40		45.63
463.15	18.19		47.35
468.15	19.01		49.10
473.15	19.86	18.48[a] 18.96[b]	50.90
478.15	20.73		52.74
483.15	21.64		54.63
488.15	22.59		56.59
493.15	23.59		58.63
498.15	24.66	23.26[b]	60.78
503.15	25.83		63.12

[a] Machado and Streett (*7*). [b] Yerlett and Wormald (*8*).

Equation 2 has been integrated with respect to T to obtain $H_T - H_{298}$, and has been divided by T and integrated (the last term numerically) with T to obtain $S_T - S_{298}$. Values of these two functions are listed in Table II. For comparison, Table II also lists $H_T - H_{298}$ values reported by Machado and Streett (*7*) and Yerlett and Wormald (*8*), after correction to a pressure of 8.3 MPa.

Examination of Table I shows excellent agreement between the heat capacities at low temperatures reported here and those reported by Machado and Streett (*7*). This is not surprising since the values reported by Machado and Streett are derived from the heat capacities of the saturated liquid reported by Carlson (*1*), which is also one of the sources from which low-temperature heat capacities reported here have been derived. However, the heat capacities above 325 K reported by Machado and Streett are derived from an extrapolation of Carlson's experimental values, and they state that errors may exceed 20% at high temperatures and pressures. At temperatures above 353.15 K Machado and Streett's heat capacities become successively more positive relative to the present measurements; at 473.15 K, the difference is 29%.

Table II shows that the current measurements supports the relative enthalpy data reported by Yerlett and Wormald (*8*) over that of Machado and Streett (*7*), at all temperatures. However, as the temperature increases, the relative enthalpies reported here increase at a faster rate than those reported by Yerlett and Wormald, until at the highest temperature the difference is nearly 6.0%. Yerlett and Wormald report their enthalpy measurements to be accurate to 0.6%. The estimated overall error of the heat capacity measurements in the present measurements is estimated to be 0.9%. While the standard deviation of the data from eq 2 is considerably greater (1.65%), the error in the enthalpies resulting from the integration of eq 2 will be much smaller. We cannot explain the significant differences between the high-temperature enthalpies calculated from the heat capacities reported in this work and those reported by Yerlett and Wormald.

Registry No. Methanol, 67-56-1.

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Vapor–Liquid Equilibria at 760 mmHg in the Ternary System Methanol–1,1-Dichloroethane–Propyl Bromide

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Vapor–liquid equilibrium at atmospheric pressure has been determined for the title ternary system. The data were correlated by various equations and the appropriate parameters are reported.

The present work was undertaken to measure VLE data for the ternary system methanol–1,1-dichloroethane–propyl bromide for which no isobaric data are available.

Experimental Section

Purity of Materials. Analytical grade methanol (99.5%+) was purchased from Frutarom; propyl bromide (99.4%) and 1,1-dichloroethane analytical grade (99.6% +) were purchased from Merck. The reagents were used without further purification after gas chromatography failed to show any significant impurities. Properties of the pure components appear in Table I.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (*1*) was used in the equilibrium determination. The experimental features have been described in previous publications (*2*). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 200 cm long and 0.2 cm in diameter, was packed with 20% OV-17, and was operated isothermally at 75 °C. Injector and detector temperatures were 220 and 230 °C, respectively. Very good separation was achieved under these conditions, and calibration analyses were carried to convert the peak ratio to the weight composition of the sample. Concentration measurements were accurate to better than ±1%. The accuracy in determination of pressure and temperature was $\Delta P = \pm 2$ mmHg and $\Delta t = \pm 0.02$ °C.

Table I. Physical Constants of Pure Components

index	compd	refractive index (20 °C)	bp(760 mmHg), °C	purity [GLC (min)]
1	methanol	1.3280^a	64.68^a	99.5
		1.3284^b	64.70^b	
2	1,1-dichloroethane	1.4138^a	57.29^a	99.6
		1.4135^b	57.28^b	
3	propyl bromide	1.4348^a	70.55^a	99.6
		1.4343^b	71.0^b	
			70.80^c	

^{a}Measured. ^{b}Reference *12*. ^{c}Reference *13*.

Results

The temperature–concentration measurements at 760 mmHg for the ternary system are reported in Table II together with the activity coefficients which were calculated from the following equation (*3*)

$$\ln \gamma_1 = \ln (Py_1/P_1^0x_1) + (B_{11} - v^L{}_1)(P - P_1^0)/RT + (P/2RT)\sum\sum y_jy_k(2\delta_{ji} - \delta_{jk}) \quad (1)$$

where

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii} \quad (2)$$

Vapor pressures P_i^0 were calculated according to Antoine's equation

$$\log P_i^0 = \alpha_i - \beta_i/(\delta_i + t) \quad (3)$$

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