$NaBO_2 \cdot 0.9H_2O$, which had an x-ray pattern of the 1:1:1 compound containing a little 1:1:4. The enlongated crystals were usually less than 0.05 mm. in length. The x-ray pattern of a sample having the composition $NaBO_2 \cdot 0.42H_2O$ after heating at 105° for 3 days in an oven was submitted to the A.S.T.M. Powder Data File.

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Low Pressure Vapor-Liquid Isotherms in the Methane–3-Methylpentane Binary System

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Vapor and liquid compositions and molar volumes are reported at temperatures of 25°, 50°, 75°, and 100° C. and at pressures up to 30 atm. The data indicate that Henry's law expressed as fugacity of methane *vs.* mole fraction dissolved methane holds closely over the pressure range covered in the study. The molar liquid volumes in every case were linear with mole fraction methane.

ACCURATE values of phase compositions and molar volumes are necessary for accurate calculations of molecular mass transport. This study was undertaken to provide information on the methane–3-methylpentane binary system for use in a study involving the experimental determination of the molecular diffusion coefficient of methane in dilute liquid solutions of 3-methylpentane.

Although methane-*n*-hexane binary phase behavior over extensive temperature and pressure ranges has been reported (*9*), no phase behavior information on the methane-3-methylpentane system has been reported previously. Methane behavior has been reported in several studies (*1, 2, 5–7*), and vapor pressure and liquid density information on 3-methylpentane has been reported by Rossini *et al.* (*8*).

EXPERIMENTAL

The equipment and the experimental techniques were the same as those used in other recent studies of binary hydrocarbon systems (*3, 4, 9–11*). In obtaining bubble point isotherms, the equilibrium cell pressure was observed directly on a dead weight gage rather than on a bourdon tube gage as was done in the previous studies. The dead weight gage was sensitive to ±0.007 atm. and was accurate to ±0.06 atm. Temperatures of the equilibrium cell were taken on a platinum resistance thermometer which was accurate within 0.02° C. of the International Platinum Scale. The equilibrium cells were borosilicate glass cylindrical tubes of 12-ml. internal volume. Each cell contained a steel ball which could be actuated by a magnet outside the cell to provide stirring. They were marked and calibrated to read volume accurate to at least ±0.01 ml. The equilibrium cells were immersed in a 3.5-liter water bath confined in a cylindrical Dewar flask.

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Bubble point isotherms were taken by precisely measured additions of gaseous methane to the equilibrium cell which had been injected previously with an accurately known amount of 3-methylpentane. The methane was added from a stainless steel bomb through displacement with mercury from a manually operated mercury pump. The pump was accurate to ±0.01 ml. Each addition of methane gas to the equilibrium cell caused the pressure inside the cell to rise. Stirring the contents of the cell with the magnetically actuated ball caused vigorous contact between the gas and liquid phases. The stirring was continued for about five minutes. The phases in the cell were then regarded to be in stable isothermal equilibrium. Readings were taken on cell pressure, liquid volume, and mass of methane added to the cell. Additional stirring over the 5-minute period never caused changes in any of the measured quantities, which was strong evidence that true equilibrium had been attained.

Dew point phase compositions and molar volumes were measured using a special dew point cell which has an internal volume of 9 ml. This cell was equipped with a capillary tube section on its lower end so that very small amounts of liquid in the cell could be read with high precision.

The experimental procedure for an isothermal dew point run was practically identical to that for the bubble point isotherms. In the case of the dew point runs, only about 0.2 ml. of 3-methylpentane was initially injected into the cell. Methane gas was added to the cell in accurately known incremental amounts. After each addition of gas, the cell contents were stirred for at least 15 minutes. Equilibrium was attained more slowly in the dew point runs owing to the smaller size of the steel balls which were inside the dew point cell.

The methane and 3-methylpentane were obtained from the Phillips Petroleum Co. Both components were pure grade materials stated to have 99% minimum purity. The methane was purified further by passing it under high pressure through a bomb packed with silica gel and a second bomb containing activated carbon. The second bomb was maintained at −40° C. in a bath of acetone and dry ice. The purified gas was thought to have a purity in excess of 99.5 mole %. The 3-methylpentane was deaerated before each experimental run and used without further purification.

RESULTS

The smoothed composition and molar volumes of the vapor and liquid phases are presented in Table I. The average deviation of the experimental liquid compositions was ±0.0010 mole fraction, ±0.05° C., and ±0.07 atm. The average deviation of the experimental vapor compositions was ±0.002 mole fraction, ±0.07° C., and ±0.10 atm. The average deviation of the experimental liquid volumes was ±0.2 ml. per gram mole.

The right-hand column of Table I presents the fugacity of methane divided by mole fraction of methane in the liquid phase. The leading value in the column represents the Henry law constant obtained from extrapolating the data at finite dilution to infinite dilution. The close agreement among the fugacity–mole fraction ratios at each temperature shows that Henry's law is obeyed in the pressure range covered in this study. The fugacities of methane in solution were obtained from accurate graphical calculation of the fugacity of pure gaseous methane using the data of Keyes and Burks (*2*), Kvalnes and Gaddy (*5*), and Michels and Nederbragt (*7*). These pure methane fugacities were used with the Lewis and Randall fugacity rule to compute the methane mixture fugacities. The pure methane fugacities calculated in this study are approximately 0.5% higher than those reported by Matthews and Hurd (*6*) but are regarded as more accurate. The use of the Lewis and Randall rule to compute the fugacity of methane in the mixtures should be accurate since the

Table I. Smoothed Compositions and Molar Volumes

	Bubble Point		Dew Point		
Pressure, Atm.	Mole fraction methane	Molar volume, ml./g. mole	Mole fraction methane	Molar volume, ml./g. mole	Fugacity Per Mole Fraction Methane, Atm.
0.2225[a]	0.000	130.66	0.000	...	194.7
5	0.0234	128.68	...	4830	...
10	0.0480	126.61	0.9510	2390	194.41
15	0.0726	124.51	0.9639	1579	193.79
20	0.0965	122.49	0.9712	1174	193.83
25	0.1202	120.46	0.9758	932.7	193.76
30	0.1440	118.45	0.9787	770.7	192.93
50° C.					
0.646[a]	0.000	135.49	0.000	...	215.9
5	0.0191	133.90	...	5240	...
10	0.0411	132.02	0.9001	2591	216.20
15	0.0630	130.17	0.9277	1717	216.68
20	0.0847	128.31	0.9451	1281	217.50
25	0.1061	126.46	0.9552	1019	217.91
30	0.1273	124.67	0.9602	845.0	217.72
75° C.					
1.427[a]	0.0000	140.96	0.000	...	231.0
5	0.0149	139.70	...	5645	...
10	0.0357	137.91	0.8410	2794	233.33
15	0.0559	136.18	0.8760	1851	231.77
20	0.0757	134.45	0.8984	1381	232.87
25	0.0949	132.80	0.9132	1100	234.94
30	0.1142	131.12	0.9233	912.3	235.78
100° C.					
2.786[a]	0.000	146.80	0.000	...	240.5
5	0.0089	146.05	...	6045	...
10	0.0297	144.36	0.7292	2989	245.10
15	0.0480	142.69	0.7810	1927	241.50
20	0.0669	141.05	0.8190	1477	241.34
25	0.0860	139.41	0.8460	1176	241.60
30	0.1049	137.78	0.8655	975.8	242.33

[a] Vapor pressure of pure 3-methylpentane reported in (*8*).

Table II. Equilibrium Vaporization Ratios of the Methane–3-Methylpentane System Compared with Those of the Methane–*n*-Hexane System

		Vaporization Ratio, Methane–3-Methylpentane		Vaporization Ratio, Methane–*n*-Hexane	
Temperature, ° C.	Pressure, Atm.	K_{CH_4}	$K_{3\text{-MP}}$	K_{CH_4}	$K_{n\text{-}C_6}$
25	10	19.81	0.0515	19.45	0.0494
	20	10.06	0.0319	9.95	0.0301
	30	6.80	0.0249	6.76	0.0240
50	10	21.90	0.1041	21.38	0.1022
	20	11.16	0.0600	11.01	0.0585
	30	7.54	0.0456	7.45	0.0443
75	10	23.56	0.1649	23.24	0.1598
	20	11.87	0.1099	11.77	0.1053
	30	8.08	0.0866	7.95	0.0830
100	10	24.55	0.2791	26.25	0.2191
	20	12.24	0.1940	12.09	0.1808
	30	8.25	0.1503	8.23	0.1388

mole fraction of methane in the gas phase at the conditions reported is in excess of 0.80 mole fraction. In this high concentration range of gaseous methane, the molar volume of the gas mixture is linear in mole fraction, and therefore, the partial molar volume of methane in the gas is trivially different from the molar volume of pure gaseous methane. The logarithm of the Henry law constant plotted against reciprocal absolute temperature was a smooth curve of decreasing negative slope with increasing temperature. This curve could not be fitted to an equation of the Valentinner type (*12*).

Table II presents the comparison of the equilibrium vaporization ratios of the methane–3-methylpentane system with those of the methane–*n*-hexane system which were obtained in a previous study (*9*). In general the comparison is very much what one would expect for isomeric systems. The methane vaporization ratios are practically identical for both systems, while the vaporization ratios of 3-methylpentane are slightly higher than those of *n*-hexane, which of course is consistent with the higher vapor pressure of 3-methylpentane.

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Pressure-Volume-Temperature Relationship for a Mixture of Difluorodichloromethane and 1,1-Difluoroethane

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The pressure-volume-temperature properties of a mixture of difluorodichloromethane and 1,1-difluoroethane in the ranges of 200 to 850 p.s.i.a., 0.027 to 0.237 cu. foot per pound and 580° to 860° R., were correlated using the Martin-Hou equation of state. Vapor pressures and liquid densities were determined to near the critical temperature (681.59° R.) from 402° to 383° R., respectively.

A MIXTURE of 26.2 weight % of 1,1-difluoroethane (Refrigerant 152a) and 73.8 weight % of difluorodichloromethane (Refrigerant 12) is commercially known as Refrigerant 500. This mixture forms a minimum boiling azeotrope at 32° F. (*9*). No published equation of state is at present available for this refrigerant mixture, and few experimental data are available on other physical properties.

The pressure-volume-temperature properties have been measured and fitted to a Martin-Hou equation of state. The vapor pressure and liquid densities have been measured over a wide temperature range and the critical properties evaluated.

EXPERIMENTAL

Sample Preparation. The purity of each component in the mixture was checked by gas chromatography and was better than 99.9 mole % pure. A sample was made by mixing weighed amounts of each component in a steel bomb which was then maintained at 32° F. All subsequent samples were drawn from the liquid phase of this bomb and the noncondensables were removed using the technique mentioned in an earlier paper (*8*). Under these conditions no significant change in composition occurs, since the original mixture is the azeotropic composition at the storage temperature. The average molecular weight of this mixture is 99.31.

Measurements of the two phase region at temperatures other than 32° F. are subject to errors, since the liquid and vapor compositions are no longer exactly the same. In order to minimize this effect in both the vapor pressure and liquid density measurements, the vapor volumes over the liquid were always less than 30% of the total volume. A check on the effect of this vapor volume on the liquid composition was made.

A cylinder was charged with a sample of the CCl_2F_2–CH_3CHF_2 mixture (26.2 weight % CH_3CHF_2) such that the liquid would occupy 50% of the container volume at 212° F. A chromatographic analysis was made of the liquid phase at 32° F., then the bomb was equilibrated at 212° F., and a sample of the liquid phase was analyzed. This showed the liquid to be within 0.2 weight % of the original composition. This represents about the detectable limit of the analytical technique. Thus under all conditions of the investigation, the liquid composition is 26.2 ± 0.2 weight % CH_3CHF_2.

Temperature Measurements. All temperature measurements were made by a calibrated platinum resistance thermometer. The resistance was measured by a Leeds and Northrup Speedomax high precision resistance recording bridge. A standard resistor was used to calibrate the bridge.