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.

The ice point resistance of the thermometer was used to check the accuracy of the recorder periodically. The resistance was constant to ±0.001 ohm, which corresponds to an accuracy of ±0.02° F.

Pressure Measurements. A closed-end mercury manometer was used for pressure measurements below 15 p.s.i.a. The mercury height was measured on a mirror back meter scale, and the readings were corrected to standard density and gravity. The accuracy of these measurements is better than 0.1%.

At higher pressures, Heise Bourdon tube gages were employed. To avoid pressure readings on the lower portion of the scale where the percentage error is the greatest, a series of overlapping pressure ranges were used. The gages were 16-inch, temperature compensated, vertically mounted and of the ranges 0 to 50, 0 to 100, 0 to 300, and 0 to 1000 p.s.i.a.

Prior to use, each Heise gage was calibrated over its entire pressure range by comparison with a Harwood controlled clearance piston gage (*4*). The accuracy of our Harwood unit is better than 0.02% for the pressure range 0 to 2000 p.s.i. All gages were accurate to better than 0.1% of the full scale value, including hysteresis, as guaranteed by the manufacturer. In most cases this error was less than 0.05% of the full scale value. Periodic recalibrations of the gages were made during the course of the work. Therefore, the uncertainty in the pressure measurements is ±0.2% or less.

Vapor Pressure. The saturated vapor pressure was measured by three different techniques depending on the pressure range. Data below the boiling point were determined by direct connection of a thermostated bomb to a closed-end mercury manometer. Above the normal boiling point and below ambient temperatures the vapor pressure was determined by direct connection of the thermostated bomb to a Heise Bourdon gage. For temperatures above ambient, the bomb was fitted with a null point diaphragm transmitter and balancing circuit (*12*).

All samples were thermostated in stirred liquid baths using various fluids at different temperatures. The bath temperatures were maintained by a proportional controller with temperature fluctuations of less than 0.05° F. corresponding to an uncertainty of less than 0.02%. The mean value was taken as the experimental temperature, since the high heat capacity of the sample cell caused a damping of the temperature fluctuations.

The effect of liquid phase composition changes were evaluated. Using the data of Pennington (*10*) the relative insensitivity of the vapor pressure to composition can be seen. In changing from 26.52 to 22.53 weight % CH_3CHF_2 the observed pressure changed only 0.09 p.s.i.a. or 0.2%. A change in composition of 0.2 weight % CH_3CHF_2 would correspond to a pressure change of only 0.005 p.s.i.a. or 0.01%. At other points on the composition-pressure curve the change is somewhat greater, but even in the extreme portions of the curve, the change is only 0.05 p.s.i.a. or 0.1% for a composition shift of 0.2 weight % CH_3CHF_2.

A check of the effect of composition change on the vapor pressure at higher pressures was also made. A charge of the CCl_2F_2-CH_3CHF_2 mixture sufficient to give 70% liquid was loaded into the vapor pressure apparatus and equilibrated at 212° F. A small addition of CH_3CHF_2 was made sufficient to change the composition by 2 weight %. This caused a change in the vapor pressure of 0.73%, thus the change of 0.2 weight % CH_3CHF_2 can be expected to cause an error of less than 0.1% in the vapor pressure.

An equation representing the experimental vapor pressure data is:

$$\log_{10} P = 7.93494 - \frac{2.351584 \times 10^3}{T} - 4.05836 \times 10^{-3} T + 2.33346 \times 10^{-6} T^2 \quad (1)$$

where

T is ° R. = (° F. + 459.69) and P is in p.s.i.a.

This equation gives a standard deviation of 0.13 for the experimental data (Table I). An extra significant figure has been kept for consistency in computation.

Liquid Density. The liquid densities were determined by a float technique which was tested on CCl_2F_2 and CCl_4 and found accurate to 0.1% over the range covered.

Calibrated hollow glass floats of various densities were sealed into a heavy-walled glass tube, the refrigerant was condensed in the tube and the end was sealed. The apparatus was thermostated to ±0.02° F. in a liquid bath, and the temperature required for each float to sink and to rise was determined. At the mean of these temperatures the density of the liquid is equal to the density of the float. To evaluate the error in the liquid densities due to composition changes, the density change for a 0.2 weight % variation was calculated. This showed an error of less than 0.1% due to this effect.

The equation used to correlate the liquid densities was than of Martin and Hou (*6*).

$$\rho_s = \rho_c + \sum_{i=1}^{n} A_1 \left[\left(1 - \frac{T}{T_c} \right)^{1/3} \right]^i \quad (2)$$

An excellent fit of the experimental data was obtained when n was 4. This fit is well within the experimental accuracy of the data which is 0.1%. The constants for the equations are shown in Table II.

PVT Measurements. The *PVT* measurements were made using a constant volume apparatus of 17.95 ± 0.01 cu. inches at 75° F. The cubical coefficient of thermal expansion for stainless steel No. 304 of 97 × 10^{-6} °$F.^{-1}$ served to correct the equipment for temperature changes. The effect of pressure on the volume was negligible. The uncertainty in the volume is 0.1% or less. The unit was constructed at this laboratory and used a pressure transducer similar to the design of Waxman and Chen (*11*). Certain modifications were made for the purpose of simplifying

Table I. Vapor Pressure

Temp., ° R.	Pressure, P.S.I.A. Obsd.	Calcd.	Dev., %[a]
401.83	6.756	6.7420	+0.21
410.74	8.643	8.6391	+0.05
426.80	13.051	13.1240	−0.56
455.71	25.74	25.692	+0.19
473.78	37.45	37.367	+0.22
491.69	52.57	52.596	−0.05
530.28	101.0	101.02	−0.02
563.54	164.5	164.47	+0.02
599.72	262.4	262.55	−0.06
635.63	396.6	396.74	−0.04
671.72	576.9	576.65	+0.04

[a] $[(P_{\text{obsd.}} - P_{\text{calcd.}})/P_{\text{obsd.}}] \times 100$. The calculated normal boiling point of the mixture using Equation 1 is −28.31 ° F.

Table II. Liquid Density

A_1 = +43.562

A_2 = +74.709

A_3 = −87.583

A_4 = +56.483

T_c = 681.59 ° R.

ρ_c = 31.00 lb./cu. ft.

Temp., ° R.	Density, Lb./Cu. Ft. Obsd.	Calcd.
383.11	87.59	87.59
451.37	81.28	81.27
512.77	74.91	74.97
564.26	68.67	68.68
606.62	62.37	62.36
638.41	56.12	56.11
660.47	49.88	49.88

the apparatus and extending its temperature range. The capacitance sensing technique was replaced with a simple electrical contact and lava packing was used throughout.

The unit was checked against the data of Douslin, Moore, and Waddington (*3*) on octafluorocyclobutane. The agreement was within the accuracy of our measurements. The *PVT* unit was thermostated in an helium air oven similar to the design of Douslin *et al.* (*2*). The temperature variation of the cell was ±0.04° F., which corresponds to an uncertainty of less than 0.01% in the temperature.

For the isochor determination, material weighing between 0.044 and 0.33 pound was distilled into the apparatus from a tared bomb. Upon completion of a run, the material was distilled back into the tared sample bomb. The initial and final weight of the sample agreed to within 1×10^{-4} pound. One hour was allowed for thermal equilibrium to be reached for the vapor density points.

Six isochors were taken with volumes varying from 0.027 to 0.237 cu. foot per pound. The data were fitted with a Martin-Hou (*5, 7*) equation of state. The constants for the equation are given in Table III. The equation shows good fit over the entire temperature-volume range with a maximum deviation of 0.26% and an average deviation of 0.07%. The fit of the data is shown in Table IV.

Table III. Constants for the Martin-Hou Equation of State

$$P_{(\text{p.s.i.a.})} = \frac{RT}{V-b} + \frac{A_2 + B_2T + C_2e^{-kT/T_c}}{(V-b)^2} + \frac{A_3 + B_3T + C_3e^{-kT/T_c}}{(V-b)^3} + \frac{A_4}{(V-b)^4} + \frac{A_5 + B_5T + C_5e^{-kT/T_c}}{(V-b)^5}$$

R = +0.10805000 [(cu. ft.)/(° R.)]/[(p.s.i.a.)/(lb.)]
$b = +6.034229 \times 10^{-3}$ $B_3 = -3.141665 \times 10^{-5}$
$k = +5.475$ $C_3 = +2.742282$
$A_2 = -4.549888$ $A_4 = -8.726016 \times 10^{-4}$
$B_2 = +2.308415 \times 10^{-3}$ $A_5 = -1.375958 \times 10^{-6}$
$C_2 = -92.90748$ $B_5 = +9.149570 \times 10^{-9}$
$A_3 = +8.660634 \times 10^{-2}$ $C_5 = -2.102661 \times 10^{-4}$

Table IV. Pressure-Volume-Temperature Relationship of the Mixture

Volume, Cu. Ft./Lb.	Temp., ° R.	Pressure, P.S.I.A. Obsd.	Pressure, P.S.I.A. Calcd.	Dev., %
0.027090	681.97	647.3	645.59	+0.26
0.027097	687.08	687.4	686.89	+0.07
0.027101	690.88	718.3	717.73	+0.08
0.027111	698.28	777.6	778.07	−0.06
0.032145	684.24	568.7	659.15	−0.07
0.032153	692.14	709.8	710.47	−0.09
0.032161	701.07	768.4	768.45	−0.01
0.032171	709.83	825.6	825.30	+0.04
0.045346	685.48	650.7	651.78	−0.17
0.045359	693.97	687.7	688.81	−0.16
0.045368	701.34	720.5	720.69	−0.03
0.045398	714.94	778.5	788.91	−0.05
0.061325	679.34	591.7	592.16	+0.07
0.061356	695.81	641.8	641.60	+0.03
0.061372	705.35	669.8	669.78	+0.02
0.061387	712.71	692.5	691.29	+0.18
0.061399	719.75	712.3	711.70	+0.07
0.061464	755.19	812.3	812.27	0.00
0.061487	767.97	848.0	847.75	+0.03
0.090077	677.38	504.5	504.59	−0.02
0.090163	709.40	562.4	562.72	−0.06
0.090227	732.91	603.5	604.07	−0.10
0.090297	759.04	648.8	648.95	−0.03
0.090352	779.56	682.7	683.53	−0.13
0.090562	857.54	811.0	810.95	0.00
0.273486	579.64	201.6	201.48	+0.06
0.237527	585.31	205.1	204.97	+0.06
0.237584	594.06	210.3	210.30	0.00
			Av. Dev.	±0.07%

Table V. Critical Properties

	This Work	Carrier (*1*)
Critical temperature, ° F.	221.9 ± 0.2°	221.1°
Critical pressure, p.s.i.a.	642 ± 1	631
Critical density, lb./cu. ft.	31.0 ± 0.1	31.1

Critical Properties. The critical temperature was determined by observation of the meniscus in a sealed glass tube which was slowly heated and cooled in a stirred liquid bath. The average value of several observations was +221.9° ± 0.2° F.

Extrapolation of the near-critical isochor to the critical temperature determined the critical pressure. This gave a value of 642 ± 1 p.s.i.a., more reliable than extrapolation of the experimental vapor pressure data because of the rapidly changing value of (dP/dT) in the critical region.

The critical density was determined by a standard rectilinear diameter plot using the liquid densities calculated from Equation 2 and saturated vapor densities calculated from the equation of state. The value determined was 31.0 pounds per cu. foot. This value, representing the critical density, was used for the constant Equation 2.

RESULTS AND DISCUSSION

Pennington (*10*) reported a value of 52.72 p.s.i.a. for the vapor pressure of this mixture at 32° F. This compares with the value of 52.60 p.s.i.a. in our work.

The vapor pressure and liquid densities were compared with the tables published by the Carrier Corp. (*1*). The vapor pressures agree to better than 0.5% from +160° to −10° F. and the deviations do not exceed 1% down to −40° F. The liquid density data agree within 0.2% with the carrier data. The critical temperature and density also show good agreement, but the critical pressure of this work is somewhat higher. A comparison of the critical properties is shown in Table V.

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