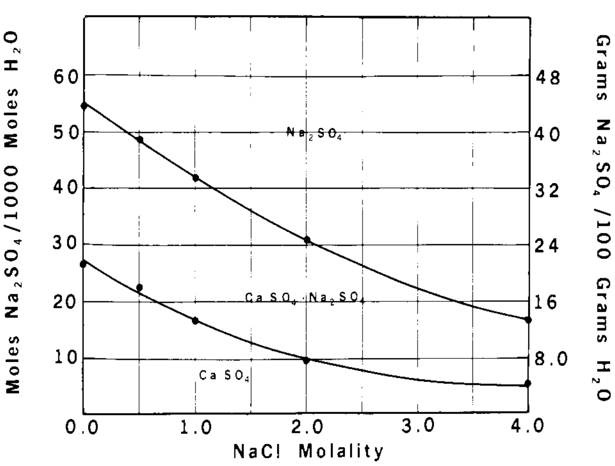

Figure 8. $CaSO_4$–Na_2SO_4 phase diagram at 100° C. and 0.0–4.0 molal NaCl

8. At this temperature, all the salts are dehydrated, leaving only $CaSO_4$, $CaSO_4 \cdot Na_2SO_4$, and Na_2SO_4. The solubility of anhydrite increases with salinity to a maximum above 2.0 molal NaCl and then remains relatively constant thereafter. The solubility of the other two salts decrease with increasing salinity.

No hemihydrate was found at any of the studied conditions except possibly at 85° and 100° C. at the lower salinities. This phase appears to be a transient one between gypsum and anhydrite.

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Pressure-Volume-Temperature Behavior of a Mixture of Difluoromethane and Pentafluoromonochloroethane

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This work presents pressure-volume-temperature properties of a mixture of 73.5 mole % difluoromethane with 26.5 mole % pentafluoromonochloroethane, commonly known as Refrigerant 504. The work includes vapor pressures from −57.72° C., the boiling point, to +66.1° C., the critical point, isochor and isotherm data from 25° to 199° C. at specific volumes between 0.7 and 9.4 cc. per gram, and liquid density data between −30° and +60° C. Correlation equations fit the data to standard deviation of ±0.35% or better, except for the liquid compressibility data which do not obey the Martin-Hou equation used for the vapor density data, and the dew point data where the standard deviation from the vapor pressure equation worsens to ±0.7%.

THE MIXTURE of 0.735 mole of difluoromethane (Refrigerant 32) and 0.265 mole of pentafluoromonochloroethane (Refrigerant 115) is commercially known as Refrigerant 504, which forms a minimum boiling azeotrope at 0° C. (*1*). This work presents its thermodynamic properties, including vapor pressures and liquid and vapor densities, with their correlating equations which include a Martin-Hou equation of state.

No experimental data have been found dealing with the vapor pressure or *PVT* properties of this mixture. Information is available for the components difluoromethane (*3*) and pentafluoromonochloroethane (*4*).

EXPERIMENTAL

Sample Preparation. Both the CH_2F_2 (Genetron 32) and the CF_3CF_2Cl (Genetron 115) were purified and degassed as previously described (*3, 4, 6*). Chromatographic analysis showed them to be better than 99.95 mole % pure.

To prepare the azeotropic mixture, exact weights of each

Table I. Methods of Measurement

Measurement	Experimental Method	Variable	Experimental Range	Accuracy, %
Vapor pressure	Manometer	P	0 to 1 bar	±0.1
		T	−57° C., 1 point	±0.05 (0.05° C.)
	Gage, direct connection	P	1 to 10 bars	±0.1
		T	−25° to 0° C.	±0.1 (0.01° C.)
	Mercury piston	T	−25° to 66° C.	±0.02 (0.02° C.)
		P	4 to 48 bars	±0.1
Equation of state	Constant volume	V	1.8 to 9.4 cc./g.	±0.1
		P	25 to 85 bars	±0.1
		T	60° to 200° C.	±0.05 (±0.05° C.)
	Mercury piston	V	0.75 to 31 cc./g.	±0.05
		P	4 to 100 bars	±0.1
		T	−25° to +75° C.	±0.02 (0.02° C.)
Density	Calibrated beads	d	1.3 to 0.8 g./cc.	±0.10
		T	33° to +58° C.	0.05 (0.05° C.)
	Liquid pressure	d	1.288 to 1.059	±0.1
	Extrapolation	T	−25° to +25° C.	±0.2 (0.2° C.)

Table II. Correlation Equations

VAPOR PRESSURE

$$\log_{10} P = A + B/T + CT + DT^2 \qquad (1)$$

P = bars
T = t ° C. + 273.16
A = 7.320321
B = 1247.326
C = -9.48559×10^{-3}
D = 1.09411×10^{-5}

EQUATION OF STATE, MARTIN-HOU

$$p = \frac{RT}{V-b} + \sum_{n=2}^{5} \frac{A_n + B_n T + C_n \exp(-KT/T_c)}{(V-b)^n} \qquad (2)$$

p = bars
V = cc./gram
T = t° C. + 273.16
T_c = 339.26° K.
R = 1.050200 cc., bar/° K, g.
b = 0.3443335 cc./g.
K = 5.475
A_2 = −1368.159
B_2 = 1.385360
C_2 = −37123.27

A_3 = 1659.606
B_3 = −1.113497
C_3 = 67195.56
A_4 = −1164.992
B_4 = 0
C_4 = 0
A_5 = −78.42037
B_5 = 1.517708
C_5 = −20825.73

DENSITY EQUATION

$$d = d_c + \sum_{i=1}^{4} A_i (1 - TR)^{i/3} \qquad (3)$$

T = t ° C. + 273.16
TR = T/T_c
d_c = 0.5177 g./cc.
T_c = 339.26° K.
A_1 = 0.73047
A_2 = 1.1093
A_3 = −1.0374
A_4 = 0.60009

Table III. Vapor Pressures

Equation 1. Bubble points standard deviation ±0.13 bar, ±0.58%
Dew points standard deviation ±0.26 bar, ±0.92%

		Bubble Points		Dew Points	
T, ° C.	P_{calcd}, Bars[a]	P_{obsd}, Bars	Dev., %	P_{obsd}, Bars	Dev., %
−57.72[b]	1.0137	1.0132	−0.05	...	...
−25.2	4.080	...	...	4.052	−0.74
−25.0	4.110	4.134	0.57	...	...
−22.26[b]	4.547	4.571	0.53	...	...
0.0[b]	9.535	9.563	0.30	...	...
0.0	9.535	9.440	−0.9	9.44	−0.9
17.0[c]	15.50	15.51	0.07	...	...
24.5	18.87	...	...	18.82	−0.26
25.0	19.11	19.20	0.45	19.14	0.15
26.41[b]	19.81	19.75	0.31	...	...
35.2	24.58	...	...	24.30	−1.17
50.0	34.50	...	...	34.10	−1.16
50.2	34.65	34.57	−0.25	...	...
60.0	42.72	42.80	0.25	42.40	−0.76
60.1	42.81	42.87	0.14	42.59	−0.52
66.1t_{crit}	48.41	48.30	−0.19	...	...

[a] Equation 1. [b] Static and boiling point measurement. [c] Liquid-vapor equilibrium study (2).

pure component were mixed together in a tared cylinder and the product was further degassed.

Apparatus and Experimental Procedures. Except as described below, these procedures are described elsewhere (*3-6*). Table I lists the several methods for procuring the measurements, with the experimental ranges used and the accuracy of the measured variables.

The high pressure window of the mercury piston unit (*3, 5*) permitted observation of bubble and dew points during the vapor pressure measurements. Segregation of the more volatile component might cause slight variations in liquid phase compositions. Hence, the same precautions were taken as in the work on the azeotrope, Refrigerant 500 (*6*), and over the measurement ranges of this work the effect should be less than 0.2%.

Both the mercury piston and the constant volume method (*6*) measured the vapor density data. Thus, both isotherms and three high temperature isochors are available for derivation of the Martin-Hou equation of state (Equation 2). The mercury piston unit also obtained specific volume-pressure isotherms in both the liquid pressure and gaseous regions. The first exists above the vapor pressure-temperature line, whereas the second is below this boundary.

Float-sink temperatures of calibrated glass beads of various densities (*6*) and extrapolation of the liquid phase specific volume-pressure isotherms to the vapor pressure-temperature (*3*) line were used to determine the density of the saturated liquids. For the critical temperature measurement, the appearance and disappearance of the liquid-vapor meniscus were observed.

Table IV. *PVT* Data on Refrigerant 504

Equation 2. Standard deviation (83 points) +0.138 bar
Standard % deviation (83 points) +0.37

T, °C.	V, Cc./G.	P_{obsd}, Bars[a]	P_{calcd}, Bars[b]	Dev., %
−15.00	0.782	100.3		
	0.793	50.30		
	0.798	25.30		
	0.802	15.30		
	0.803	10.30		
	0.805	7.30		
	0.807	6.30		
	42.150	5.60	5.610	−0.18
0.00	0.816	100.90		
	0.848	10.30		
	0.8475	9.44		
	28.156	8.50	8.550	−0.58
	38.382	6.50	6.584	−1.29
25.00	0.885	100.9		
	0.885	100.6		
	0.935	25.70		
	0.938	20.70		
	0.942	20.90		
	0.944	19.22		
	11.881	18.80	18.853	−0.28
	15.402	15.80	15.776	0.14
	15.402	15.70	15.776	−0.49
	26.617	10.50	10.198	2.87
35.20	0.906	100.60		
	0.980	30.60		
	0.987	25.60		
	0.991	24.60		
	9.128	23.70	23.788	−0.37
	9.857	22.75	22.743	0.03
	11.403	20.76	20.735	0.12
	16.553	15.80	15.824	−0.15
40.00	0.929	100.30		
	0.977	50.30		
	1.014	30.30		
	1.019	28.30		
	8.042	26.40	26.449	−0.18
	9.251	24.40	24.442	−0.17
	10.580	22.40	22.469	−0.30
	12.117	20.40	20.491	−0.44
	27.605	10.50	10.572	−0.68
52.00	0.980	100.6		
	1.071	50.60		
	1.126	39.60		
	1.147	36.60		
	1.149	36.15		
	5.057	35.75	35.891	−0.39
	5.363	35.17	35.174	−0.01
	7.262	30.70	30.604	0.31
	13.081	20.80	20.706	0.45
	13.249	20.42	20.506	−0.41
	29.143	10.50	10.583	−0.79
60.00	1.026	100.6		
	1.198	47.60		
	1.260	43.60		
	1.313	42.70		
	4.055	41.70	41.609	0.21
	4.428	40.70	40.608	0.22
	7.922	30.70	30.731	0.09
65.00	1.056	100.7		
	1.323	50.70		
	1.355	49.70		
	1.399	48.70		
	1.429	48.20		
	1.484	47.70		
	2.753	47.20	47.057	0.30
	3.079	46.60	46.571	0.06
	3.486	45.70	45.638	0.13
	4.994	40.70	40.721	−0.05
	8.291	30.80	30.782	0.05
	14.042	20.80	20.866	−0.31
68.00	1.083	100.6[c]		
(> T_c)	1.881	50.60	50.425	0.34
	2.674	49.60	49.422	0.35
	3.078	48.65	48.514	0.28
	3.258	48.15	48.011	0.28
	3.423	47.65	47.506	0.30
	3.563	47.15	47.050	0.21
	3.704	46.66	46.571	0.19
	3.979	45.66	45.590	0.15
	5.288	40.68	40.681	−0.00
	8.513	30.70	30.776	−0.24
	10.890	25.80	25.798	0.00
70.00	1.096	100.6[c]		
	1.317	60.60	60.507	0.15
	1.448	55.60	55.570	−0.05
	2.375	51.65	51.613	−0.07
	3.134	49.65	49.620	−0.06
	3.685	47.66	47.664	0.00
	4.180	45.66	45.723	−0.13
	5.421	40.70	40.819	−0.29
	8.637	30.70	30.819	−0.38
	11.003	25.80	25.853	−0.20
75.00	1.137	100.6[c]		
	1.594	60.60	60.950	−0.57
	2.050	57.30	57.330	0.05
	2.445	55.70	55.630	0.12
	3.227	52.34	52.313	−0.05
	3.580	50.70	50.695	0.09
	4.643	45.70	45.754	−0.11
	5.803	40.70	40.816	−0.28
	8.958	30.70	30.861	−0.52
	11.339	25.80	25.876	−0.29
	11.511	25.40	25.575	−0.68
	15.087	20.42	20.555	−0.65
	31.939	10.50	10.597	−0.92
45.13	9.4197	25.062	25.033	0.116
60.00	9.4273	27.269	27.420	−0.56
70.05	9.4324	28.896	28.974	−0.271
89.99	9.4426	31.909	31.947	−0.119
150.07	9.4731	40.438	40.339	0.246
199.92	9.4985	47.126	46.917	0.444
90.77	3.8577	56.661	56.741	−0.142
107.97	3.8613	64.418	64.406	−0.018
119.88	3.8638	69.534	69.554	−0.030
140.01	3.8679	77.911	78.026	−0.15
70.06	1.8764	52.786	52.738	0.092
79.97	1.8774	63.921	63.849	0.112
89.90	1.8784	74.987	75.002	−0.020
100.03	1.8794	86.501	86.392	0.126

[a] Where no P_{calcd} occurs, points represent compressed liquid data. [b] Calculated from Equation 2. [c] Not fitted by Equation 2.

RESULTS AND DISCUSSION

The equations of Table II summarize the experimental data of Tables III to V. For vapor pressure, Equation 1 correlates the bubble point pressures with a standard deviation of ±0.13 bar and a standard per cent deviation of ±0.58%. As might be expected in cases where the mixture diverges from the azeotropic conditions, the dew point pressures are somewhat lower than those calculated from Equation 1, particularly above 25° C., and the standard per cent deviation worsens to ±0.92%. The agreement of the dew and bubble points at −25° C. is probably within the over-all experimental error. The equation also agrees well with an earlier Allied data point taken in a liquid-vapor equilibrium study. The equation predicts a boiling point of −57.21° C. compared to −57.22° C. observed at Allied in an earlier study using boiling point tubes.

Table IV presents measured isotherms and isochors describing specific volumes of the compressed vapor and liquid at various temperatures and pressures. Agreement with the Martin-Hou relation (Table II, Equation 2) is also shown. The equation correlates the vapor density data up to 1.4 times the critical density with a standard deviation of ±0.14 bar and a standard per cent deviation for 83 points of ±0.37%. It does not correlate the liquid compressibility data except near the critical density. Hence, Table IV presents computed data only for the points at the higher specific volumes where the Martin-Hou equation (Equation 2) applies.

Equation 3 of Table II represents the liquid density data from the density beads (Table V) to within ±0.13% standard per cent deviation. Liquid densities obtained by extrapolating the liquid compressibility curve to vapor pressure conditions agree well with the calculated values at temperatures far enough from the critical. Increased curvature of the liquid isotherms sets in near the vapor pressure–temperature curve, which makes the extrapolation less accurate.

The measured critical temperature in the mercury piston equipment is 66.1° ± 0.1° C., in good agreement with a value of 66.4° ± 0.2° C. obtained previously by Allied from the conventional sealed tube method. The measured critical pressure from the mercury piston unit is 48.3 ± 0.15 bars. From a rectilinear diameter line plot the critical density is 0.518 ± 0.005 grams per cc. due to extrapolated error. The data for the rectilinear diameter line resulted from the liquid density equation and from implicit solutions of the Martin-Hou Equation 2, at the desired vapor pressure conditions. When Equation 2 is solved implicitly for the specific volume at 66.10° C. and 48.30 bars, the critical constants, a value of 1.9318 cc. per gram or 0.5177 gram per cc. results, in good agreement with 0.518 gram per cc. from the rectilinear diameter line extrapolation.

Table V. Liquid Density of Refrigerant 32/115 Azeotrope

t, ° C.	D,G./Cc. Obsd.	D,G./Cc. Calcd.	$d_{obsd} - d_{calcd}$	$\frac{100(d_{obsd} - d_{calcd})}{d_{calcd}}$
		Method, Beads		
−32.28	1.3018	1.3015	0.0003	0.01
5.30	1.2005	1.2015	−0.0010	−0.08
17.78	1.1000	1.0986	0.0014	0.12
35.27	0.9998	1.0006	−0.0008	−0.07
48.83	0.8993	0.8993	0.0000	0.00
58.02	0.7992	0.7991	0.0001	0.01
		Method, Liquid Compressibility Extrapolation		
−25.0	1.2887	1.2761	0.0126	0.98
−15.00	1.2379	1.2394	−0.0015	−0.11
0.00	1.1799	1.1796	0.0003	0.02
25.00	1.061	1.061	−0.000	0.00
25.00	1.064	1.061	0.003	0.27
35.20	1.008	1.001	0.007	0.70
40.00	0.979	0.969	0.010	1.0
50.20	0.887	0.887	0.000	0.00
52.00	0.864	0.869	−0.005	−0.61
60.00	0.784	0.769	0.015	1.8

Standard deviation, bead points ±0.13%.
Standard deviation, all points ±0.68%.

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