Measurements of Pressure–Volume–Temperature Properties of 1,1,2,2-Tetrafluoroethane

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The experimental vapor pressures and pressure–volume–temperature (*PVT*) properties of an important alternative refrigerant, 1,1,2,2-tetrafluoroethane (HFC-134), have been measured by means of the constant-volume method coupled with expansion procedures in an extensive range of temperatures, pressures, and densities. One hundred seventeen *PVT* property data were measured along 14 isochores in a range of temperatures from 318 to 443 K, pressures from 0.4 to 9.8 MPa, and densities from 18 to 1103 kg/m^3. Fifty-one vapor pressures were also measured at temperatures from 303 K to the critical temperature. The uncertainties of temperature and pressure measurements are less than ±10 mK and ±3.2 kPa, respectively, while the uncertainty of density values is less than ±0.11%. The purity of the sample used is 99.98 wt %. Saturated liquid/vapor densities are expected to be accurate within ±0.4% including the uncertainties due to the extrapolation procedure.

Introduction

The hydrofluorocarbon 1,1,2,2-tetrafluoroethane (HFC-134) has zero ozone depletion potential because it contains no chlorine atoms. There is an increasing interest in hydrofluorocarbons as alternatives for chlorofluorocarbons. However, there have been few measurements on the thermodynamic properties of HFC-134.

In the present study, 117 pressure–volume–temperature (*PVT*) values and 51 vapor pressures were measured in addition to 9 saturated liquid/vapor densities. These data will contribute to the development of an equation of state which will cover the entire fluid phase of this important refrigerant.

Experimental Section

The isochoric method coupled with expansion procedures was used for measuring vapor pressures and *PVT* properties. The experimental apparatus shown in Figure 1 is composed of a sample cell (A), an expansion cell (B), a differential pressure detector (C), a platinum resistance thermometer calibrated on ITS-90 (G), a thermostated bath (H), temperature control/measuring devices, and pressure measuring instruments.

The inner volumes of the sample cell and expansion cell were carefully calibrated by using pure water; they were about 283 and 55 cm^3, respectively. The temperature in the thermostated bath filled with silicone oil was controlled within ±3 mK. After thermal equilibrium between the sample and the heat transfer oil in the bath, the pressure remained constant and the temperature and the pressure of the sample fluid were measured.

When a series of measurements along one isochore was completed, we expanded the sample fluid to the expansion cell with the fluid in the single phase to obtain another isochore. The valves between the sample cell and expansion cell were closed when the temperature and the pressure became stable. The experimental procedure and apparatus have been reported by Takaishi et al. (*1*, *2*). In our previous publications, we reported the *PVTx* measurements for the chlorodifluoromethane (HCFC-22) + dichlorodifluoromethane (CFC-12) system (*3*), chlorodifluoromethane (HFC-22) + 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114) system (*4*), bromotrifluoromethane (Halon 1301) + 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114) system (*5*), 1,1-difluoroethane (HFC-152a) + 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114) system (*6*), 1-chloro-1,1,2,2,2-pentafluoroethane (CFC-115) + 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114) system (*7*, *8*), and chlorodifluoromethane (HCFC-22) + 1-chloro-1,1-difluoroethane (HCFC-142b) system (*9*).

The experimental errors of the present measurements are estimated to be not greater than ±10 mK in temperature, ±3.2 kPa in pressure, and ±0.11% in density. The sample purity we used was 99.98 wt %.

Results

In the present study, 117 *PVT* data were measured along 14 isochores at temperatures from 318 to 443 K, pressures from 0.4 to 9.8 MPa, and densities from 18 to 1103 kg/m^3. Figure 2 shows the distribution of the present *PVT* data on a pressure–temperature plane. It should be noted that the present *PVT* property measurements provide the first set of data for HFC-134 in the entire fluid phase. Fifty-one vapor pressures, from 303 K to the critical temperature, as well as nine saturated liquid/vapor densities were also obtained.

All measured data are tabulated in Tables I–III with temperatures of ITS-90.

Discussion

The measured vapor pressures were correlated by a simple function of temperature as follows:

$$\ln P_r = (1/T_r)\{A(1 - T_r) + B(1 - T_r)^{1.5} + C(1 - T_r)^3\} \quad (1)$$

$$P_r = P/P_c \qquad T_r = T/T_c$$

$$P_c = 4.64 \text{ MPa} \qquad T_c = 391.97 \text{ K}$$

$$A = -7.4035 \qquad B = 1.4852 \qquad C = -4.3270$$

where P and T denote saturation vapor pressure and temperature, whereas P_c and T_c are the critical pressure and the critical temperature, respectively. The critical parameters estimated by Maezawa et al. (*10*) for HFC-134 were used in the present study.

Figure 3 shows the vapor pressure curves of dichlorodifluoromethane (CFC-12) (*11*) and their alternatives. This figure shows that the vapor pressures of 1,1,2,2-tetrafluoroethane (HFC-134) are always lower than those of 1,1,1,2-tetrafluoroethane (HFC-134a) (*12*), 1,1-difluoroethane (HFC-152a) (*13*), and dichlorodifluoromethane (CFC-12). And, at higher temperatures, the vapor pressure curve of 1,1,2,2-tetrafluoroethane (HFC-134) is very close to that of dichlorodifluoromethane (CFC-12). Figure 4 shows the pressure deviations from eq 1

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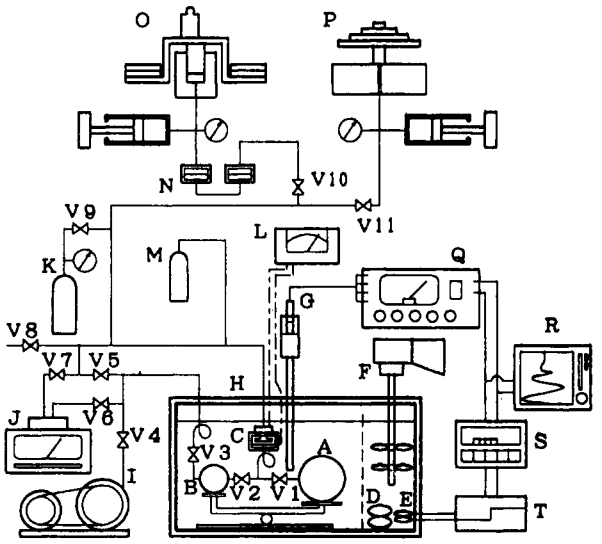

Figure 1. Experimental apparatus: (A) sample cell; (B) expansion cell: (C) differential pressure detector; (D) main heater; (E) auxiliary heater; (F) stirrer; (G) platinum resistance thermometer; (H) thermostated bath; (I) vacuum pump; (J) bourdon tube differential pressure gauge; (K) nitrogen cylinder; (L) electric resistance detector; (M) nitrogen gas damper; (N) oil–gas separator; (O) oil-operated dead weight pressure gauge; (P) air piston type dead weight pressure gauge; (Q) thermometer; (R) pen recorder; (S) PID controller; (T) dc power supply; (V1)–(V11) valves.

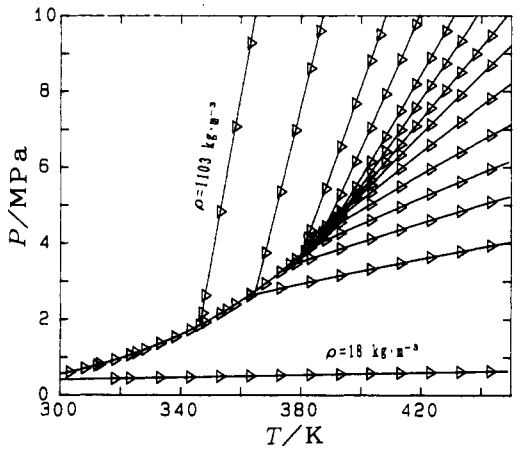

Figure 2. Distribution of the present measurements.

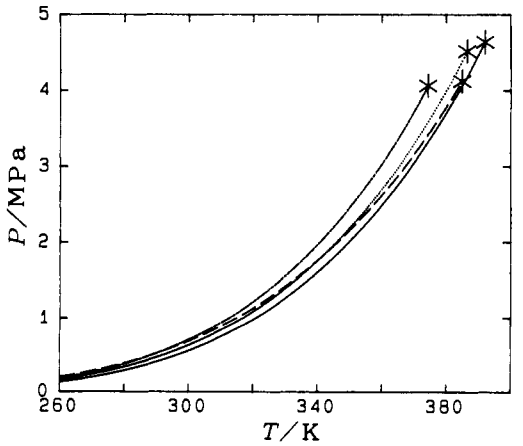

Figure 3. Vapor pressure curves of several refrigerants: (—) 1,1,2,2-tetrafluoroethane (HFC-134), (-···-) 1,1,1,2-tetrafluoroethane (HFC-134a), (···) 1,1-difluoroethane (HFC-152a), (- - -) Dichlorodifluoromethane (CFC-12).

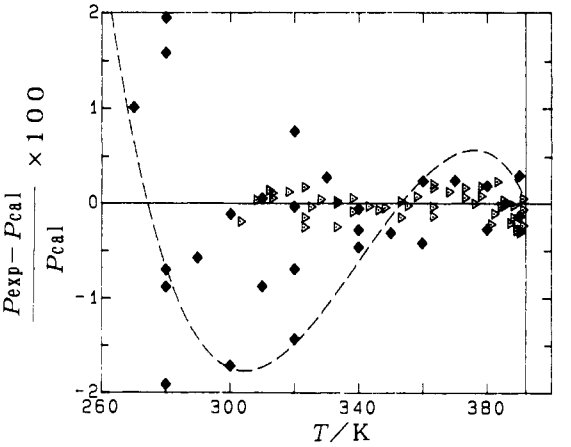

Figure 4. Deviation of vapor pressure measurements from eq 1: (▷) this work, (◆) Maezawa et al., (—) eq 1, (- - -) Maezawa et al.

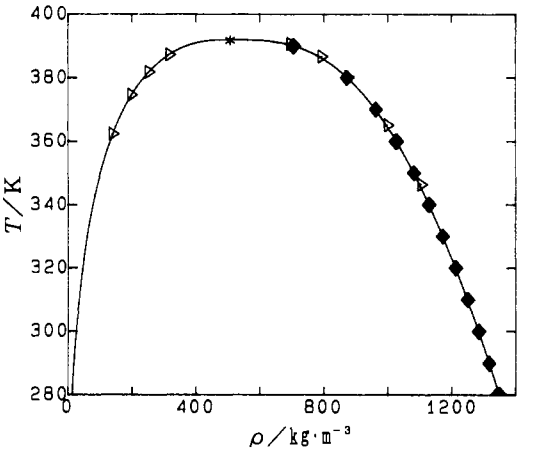

Figure 5. Distribution of the saturated vapor and liquid density measurements: (▷) this work, (◆) Maezawa et al., (—) Maezawa et al.

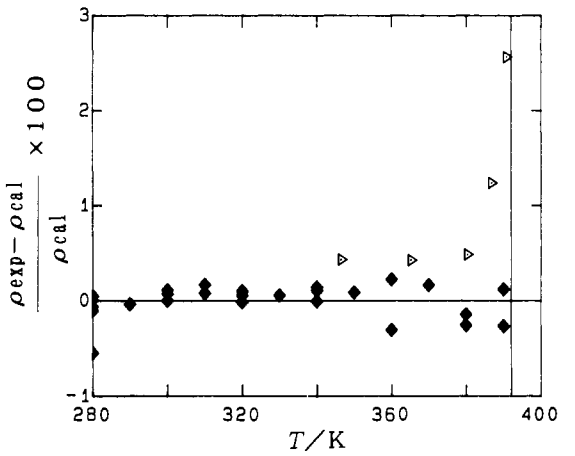

Figure 6. Comparison of the measured densities of saturated liquid: (▷) this work, (◆) Maezawa et al., (—) Maezawa et al.

which reproduces the present measurements within ±0.3%. The vapor pressure correlation reported by Maezawa et al. shows systematic deviation from the present correlation with the maximum deviation of about 1.8% at about 300 K.

We determined nine saturated liquid/vapor densities by the breaking point of each isochore graphically on a pressure–temperature plane. Figure 5 shows the distribution of the saturated densities depicted on the temperature–density plane. The saturated liquid density curve is calculated from the correlation reported by Maezawa et al. (*10*). Because of the difficulty in finding the breaking points along the isochores in the

Table I. *PVT* Properties for HFC-134

no.	ρ/(kg·m^{-3})	T^a/K	P/MPa	no.	ρ/(kg·m^{-3})	T^a/K	P/MPa	no.	ρ/(kg·m^{-3})	T^a/K	P/MPa
1	18.12	318.120	0.4352	40	251.40	443.136	5.9552	79	629.39	413.133	6.9930
2	18.12	323.128	0.4446	41	317.33	388.123	4.2891	80	629.22	418.132	7.5731
3	18.11	333.149	0.4607	42	317.25	393.129	4.5438	81	629.05	423.130	8.1589
4	18.10	343.135	0.4775	43	317.09	403.131	5.0268	82	628.87	428.134	8.7428
5	18.10	353.124	0.4925	44	316.92	413.133	5.4965	83	628.70	433.135	9.3360
6	18.09	363.129	0.5080	45	316.76	423.129	5.9556	84	695.23	391.138	4.5904
7	18.08	373.114	0.5236	46	316.59	433.131	6.4012	85	695.15	393.128	4.8362
8	18.07	383.153	0.5391	47	316.43	443.138	6.8454	86	694.96	398.115	5.4713
9	18.06	393.128	0.5544	48	399.35	391.132	4.5501	87	694.77	403.126	6.1484
10	18.05	403.110	0.5712	49	399.31	393.128	4.6878	88	694.58	408.121	6.8123
11	18.04	413.107	0.5858	50	399.11	403.129	5.3360	89	694.39	413.081	7.4929
12	18.03	423.131	0.6021	51	398.90	413.128	5.9676	90	694.19	418.117	8.1895
13	18.03	433.139	0.6172	52	398.69	423.132	6.5860	91	693.99	423.131	8.8902
14	18.02	443.137	0.6332	53	398.48	433.140	7.1977	92	693.80	428.146	9.5959
15	138.92	363.126	2.6250	54	398.27	443.137	7.8091	93	793.31	387.125	4.2781
16	138.85	373.120	2.8179	55	483.42	392.124	4.6532	94	793.27	388.129	4.4404
17	138.78	383.127	2.9893	56	483.40	393.120	4.7379	95	793.05	393.124	5.2804
18	138.71	393.127	3.1559	57	483.15	403.117	5.5379	96	792.82	398.127	6.1487
19	138.65	403.129	3.3173	58	482.89	413.114	6.3328	97	792.59	403.136	7.0387
20	138.58	413.129	3.4780	59	482.63	423.130	7.1266	98	792.36	408.135	7.9329
21	138.51	423.138	3.6340	60	482.37	433.137	7.9073	99	792.14	413.134	8.8537
22	138.44	433.139	3.7899	61	482.11	443.134	8.6904	100	791.91	418.131	9.7553
23	138.37	443.134	3.9434	62	552.32	392.132	4.6520	101	875.48	382.113	4.1369
24	197.45	378.130	3.4574	63	552.29	393.144	4.7426	102	875.42	383.112	4.3386
25	197.40	383.131	3.5957	64	552.14	398.122	5.2003	103	875.17	388.129	5.4326
26	197.30	393.125	3.8609	65	552.00	403.111	5.6649	104	874.91	393.130	6.5457
27	197.20	403.129	4.1189	66	551.85	408.099	6.1354	105	874.65	398.116	7.6749
28	197.10	413.127	4.3581	67	551.70	413.138	6.6086	106	874.39	403.128	8.8163
29	197.00	423.130	4.6057	68	551.55	418.130	7.0850	107	874.23	406.121	9.5034
30	196.90	433.137	4.8492	69	551.40	423.161	7.5634	108	999.49	368.125	3.7518
31	196.80	443.133	5.0880	70	551.25	428.150	8.0337	109	999.17	373.125	5.3467
32	252.19	382.128	3.8448	71	551.10	433.136	8.5122	110	998.86	378.131	6.9733
33	252.17	383.121	3.8967	72	550.95	438.141	8.9905	111	998.54	383.125	8.6097
34	252.11	388.124	4.0848	73	550.80	443.195	9.4739	112	998.35	386.125	9.5983
35	252.05	393.131	4.2670	74	630.11	392.126	4.6493	113	1103.91	347.090	2.1724
36	251.92	403.129	4.6111	75	630.08	393.129	4.7539	114	1103.83	348.129	2.6296
37	251.79	413.126	4.9570	76	629.91	398.127	5.2925	115	1103.46	353.115	4.8291
38	251.66	423.134	5.2959	77	629.74	403.127	5.8490	116	1103.08	358.149	7.0706
39	251.53	433.133	5.6241	78	629.57	408.127	6.4170	117	1102.71	363.106	9.2830

[a] T = temperature on ITS-90.

Table II. Saturation Vapor Pressures for HFC-134

no.	T/K	P/MPa	no.	T/K	P/MPa
1	312.149	0.7933	27	323.105	1.0647
2	323.125	1.0618	28	328.138	1.2083
3	346.133	1.8460	29	333.146	1.3659
4	363.122	2.6520	30	338.113	1.5360
5	313.125	0.8148	31	343.119	1.7253
6	323.135	1.0656	32	348.121	1.9299
7	333.126	1.3656	33	353.123	2.1538
8	338.126	1.5387	34	358.113	2.3958
9	363.129	2.6615	35	363.140	2.6611
10	353.125	2.1502	36	368.117	2.9415
11	363.102	2.6537	37	373.115	3.2485
12	373.122	3.2456	38	378.123	3.5802
13	378.089	3.5742	39	383.129	3.9406
14	384.128	4.0049	40	388.127	4.3175
15	385.125	4.0812	41	391.116	4.5687
16	386.125	4.1597	42	325.127	1.1191
17	388.123	4.3115	43	355.125	2.2470
18	382.126	3.8532	44	385.125	4.0835
19	389.127	4.3872	45	389.125	4.3873
20	390.126	4.4701	46	390.130	4.4691
21	391.124	4.5564	47	376.124	3.4386
22	391.112	4.5630	48	387.127	4.2294
23	303.132	0.6097	49	381.121	3.7762
24	308.122	0.7071	50	323.107	1.0602
25	313.139	0.8147	51	333.093	1.3608
26	318.140	0.9340			

Table III. Densities of the Saturated Vapor (ρ'') and Liquid (ρ') for HFC-134

no.	T/K	ρ''/(kg·m^{-3})	no.	T/K	ρ'/(kg·m^{-3})
1	362.31	138.9	5	390.71	695
2	374.58	197.5	6	386.72	793
3	381.81	252.2	7	380.27	876
4	387.29	317.3	8	365.09	1000
			9	346.39	1104

critical region, we could not determine these densities. Figure 6 shows the deviations of the saturated liquid density values from the correlation reported by Maezawa et al. The present saturated liquid densities are systematically greater than the correlation by 0.4% at temperatures below 380 K, while the deviations increase with increasing temperature toward the critical temperature.

Conclusion

One hundred seventeen *PVT* property values along 14 isochores have been measured. The present experimental *PVT* values are considered as a first set of data that covers a wide range of the state parameters including both vapor and liquid phases for this important alternative refrigerant.

Fifty-one vapor pressures have also been measured. The vapor pressure correlation which is effective for temperatures between 300 K and the critical temperature has been developed, on the basis of the measurements reported by the present study and Maezawa et al. (*10*).

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Registry No. HFC-134, 359-35-3.

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Phase Diagram of the Ternary System NaBr/CsBr/H_2O Elucidated by Mechanochemical Equilibration

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Mechanochemical equilibration of the ternary system NaBr/CsBr/H_2O was investigated using a ball mill which is a closed system. Products obtained by grinding mixtures with different molar ratios of NaBr, CsBr, and H_2O were identified by X-ray diffraction, IR spectroscopy, and thermal analysis. The water content of the different species in the mixture was determined by thermogravimetry. The products of grinding are solid solutions of hydrated NaBr in CsBr, $Cs_{1-x}[Na(H_2O)]_xBr$ ($x \leq 0.48$), the hydrated double salt $Cs[Na(H_2O)]_2Br_3$, and $NaBr \cdot 2H_2O$. The phase diagram of the NaBr/CsBr/H_2O system was constructed for that part in which only solids exist in the equilibrium state. From the phase diagram it is obvious that the double salt cannot be crystallized from aqueous solutions.

Introduction

It has been previously shown that by ball mill grinding of NaBr and CsBr in the presence of water, with the molar ratio 2:1:2, a hydrated double salt $Cs[Na(H_2O)]_2Br_3$ is obtained (*1*). If the amount of NaBr is not sufficient for the formation of the double salt, or if NaBr and CsBr are ground in a mortar, which is an open system in which the salts are in contact with the atmosphere, a solid solution of H_2O and NaBr in CsBr crystals is obtained (*2*). In analogy with the ternary system NaCl/CsCl/H_2O (*3-7*), it has been suggested that the hydrated solid solution of NaBr in CsBr has the general formula $Cs_{1-x}[Na(H_2O)]_xBr$ (*2*).

We recently found that mechanochemical equilibration can be used as a method for the construction of a phase diagram of the ternary system NaCl/CsCl/H_2O, for that part of the diagram in which all components were in the solid state (*8*). In the present paper we report on the construction of a phase diagram of the ternary system NaBr/CsBr/H_2O for that region of the diagram where all components were in the solid state. In this system, in addition to NaBr, CsBr, $Cs[Na(H_2O)]_2Br_3$, and $Cs_{1-x}[Na(H_2O)]_xBr$, also sodium bromide dihydrate, $NaBr \cdot 2H_2O$, must be taken into consideration. In addition, the IR spectrum of the double salt which has not yet been described in the literature is described in this paper.

Experimental Section

Chemicals. The alkali-metal halides were of Suprapur grade, supplied by Merck.

Ball Mill Grinding. The ball mill (Retsch Model S1) was equipped with an agate cell of 50 mL and six agate balls. Mixtures of NaBr and CsBr (total amount 0.500-8.500 g) in different ratios were ground in the ball mill (640-720 rpm) for 24 h, in the presence of different amounts of water. After the first 60 min, the grinding was stopped for a short time and the mixture was thoroughly homogenized. The ground mixtures were allowed to stand in closed bottles at room temperature for 7 days before they were analyzed.

The laboratory temperature was 25 °C.

Aging of Mixtures Containing NaBr, CsBr, and H_2O (Static Equilibration). Mixtures containing 1.7025 g of CsBr, 0.4116,

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