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pvT Measurements on 1-Chloro-1,2,2,2-tetrafluoroethane (R124) along the Gas−Liquid Boundary Curve between 293 K and 395 K and in the Liquid State from 120 K to 268 K

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The densities of both the vapor and liquid of 1-chloro-1,2,2,2-tetrafluoroethane along the phase boundary from 293 K to 395 K and in the liquid phase from 120 K to 268 K at pressures to 4.5 MPa have been measured. The measurements along the phase boundary curve were made with an apparatus that allows the simultaneous determination of liquid and vapor densities using Archimedes' principle. The relative measurement uncertainties of the vapor pressure and the liquid and the vapor densities of R124 (mole fraction of impurities: less than 0.2%) at 373 K are $\pm 1 \times 10^{-4}$, $\pm 5 \times 10^{-4}$, and $\pm 1 \times 10^{-3}$, respectively. For the measurements in the liquid single-phase region along 11 quasi-isochores at pressures up to 4.5 MPa an isochoric apparatus was used. The relative measurement uncertainty of $pv/(RT)$ is less than $\pm 1 \times 10^{-3}$ (95% confidence level). In addition, the vapor pressure in the temperature range from 120 K to 273 K was measured. Correlation equations are presented for reproducing the vapor pressures, liquid densities, and vapor densities. The results are compared with those of recent publications.

1. Introduction

For the determination of equations of state, accurate measurements of the liquid and gaseous densities as well as of the saturation pressure as a function of temperature are acquired using various apparatus previously described, which have proved capable of providing measurements of high accuracy. The quality of the samples is of great significance for the quality of the data. R124 was supplied by DuPont. At the "Institut für Thermodynamik, Universität Hannover", Germany, the fluid was purified using rectification and the purity was measured using gas chromatography. The mole fraction of impurities was found to be less than 0.2%.

2. Experimental Section

A detailed description of the setup for the measurement of the saturated pressures and densities is given by Blanke et al. (1995). The system consists of a component for the measurement of the density in the liquid phase, another quite similar one for gas density measurement, instruments for the adjustment and measurement of the saturation pressure, and a component for temperature stabilization and measurement. A schematic diagram is given in Figure 1. The main components of the densitometers are a microbalance, a magnetic suspension coupling (Wagner et al., 1995), and the sinker. The uncertainty of the temperature measurement is better than 5 mK, and that of the saturated vapor pressure measurement $[(0.2\ \text{kPa})^2 + (4 \times 10^{-5}p)^2]^{1/2}$.

To avoid condensation on the sinker for the measurement of the vapor density, the temperature of the measuring cell in question was always kept slightly higher than the temperature of the cell containing the liquid. For each measurement, at least twice a temperature difference of about 0.9 K, 0.6 K, and 0.3 K was adjusted. Equilibrium was achieved when the pressure (always the same) was stable. Quite similar to the virial expansion

$$p/(RT) = 1/V_m + B/V_m^2 + C/V_m^3 + D/V_m^4 \qquad (1)$$

the vapor density on the liquid−gas boundary curve was obtained using

$$1/T = a\rho + b\rho^2 + c\rho^3 + d\rho^4 \qquad (2)$$

where p is the pressure, R is the gas constant, T is the temperature, V_m is the molar volume, B, C, and D are the virial coefficients, ρ is the density, and a, b, c, and d are adjustable coefficients. For this small temperature range of less than 1 K, the virial coefficients were treated as constant. In the case of another ethane-based refrigerant (R134a), this was tested using the fundamental equation of Tillner-Roth and Baehr (1994). In the case of the measurements under consideration, the relative differences in the extrapolation to the saturation temperature $T < 383$ K will be less than 6×10^{-4}, if the first two, three, or four terms on the right-hand side of eq 2 are taken into account. At 395 K, the relative difference between the three- and four-term approximation is 2×10^{-3}.

The saturated liquid density was measured to 383 K only. In the next point of measurement, the thin stainless steel wire 0.05 mm in diameter supporting the sinker failed. The vapor pressure from 120 K to 273 K was measured using a setup with a liquid nitrogen evaporation cryostat. The uncertainty of the temperature measurement is 2 mK, and that of the pressure measurement is estimated to be $3 \times 10^{-4}p_s$, but not less than 10 Pa (95% confidence level).

For the *pvT* measurements in the same temperature range, an apparatus was used which allows precision measurements to be carried out by the constant volume method and has been described by Blanke and Weiss (1992, 1996) (Figure 2). With this method of measurement, a specified amount of gas is added to the thermostatted cell of fixed volume; subsequently, the pressures at various temperatures are measured. The measured values lie on a quasi-isochore to be found, in these investigations, in the

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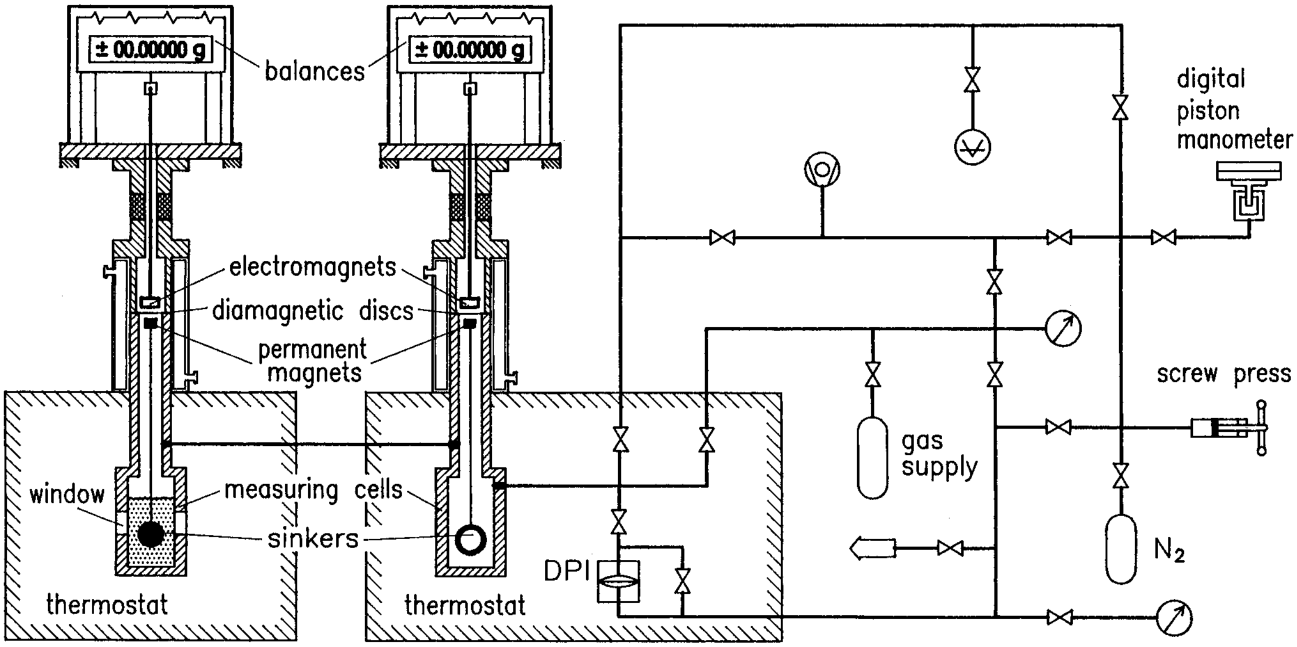

Figure 1. Schematic diagram of the apparatus for $p\rho'\rho''T$ measurements along the gas–liquid saturation curve.

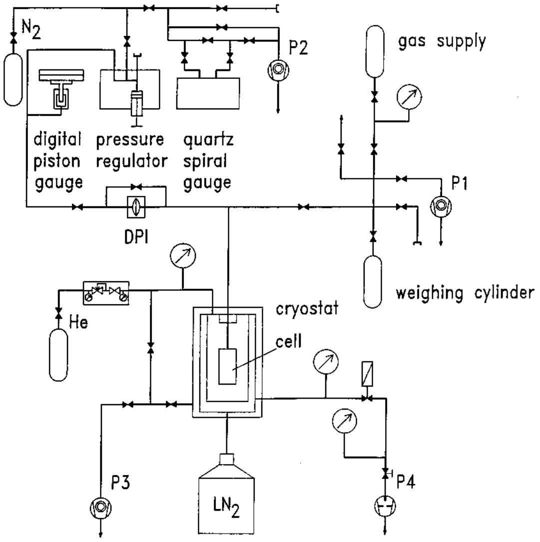

Figure 2. Isochoric $p\rho'T$ apparatus for T < 268 K.

liquid single-phase region. The density of the fluid is the quotient of its mass and the volume of the cell which is a function of pressure and temperature. To determine the mass, the gas from the cell is allowed to condense into a weighing cylinder which is cooled with liquid nitrogen. The relative uncertainty of the temperature measurement is 2×10^{-5}, the relative uncertainty of the pressure measurement 1×10^{-4}, and that of the density measurement less than 1×10^{-3}.

The triple-point temperature reported in the manufacturer's data sheet is 74 K (McLinden, 1990). This value seems anomalously low compared to the other ethane based refrigerants. It was not possible to find the triple point in the temperature range 50 K to 120 K using the apparatus described by Blanke and Weiss (1992). Therefore, the behavior of the liquid phase was visually observed from 77 K to 120 K. At lower temperatures, the fluid became very viscous. At about 90 K, a flow could no longer be observed but the specimen remained transparent. R124 was assumed to be in a glassy state. For further investigation, the fluid was filled into a glass tube 10 mm in diameter and cooled to 40 K using a refrigeration cryostat. The temperature was measured using a Pt 100 Ω thermometer immersed in the fluid. After switching off the cryostat, the specimen slowly heated up due to heat transfer along the glass tube. At 76.5 K, a phase transition was observed; the corresponding enthalpy difference was very small compared to melting enthalpies of other refrigerants. As a result, and also due to the large specific heat capacity of the measuring cell made from copper, the transition could not be detected in the triple-point apparatus (Blanke and Weiss, 1992).

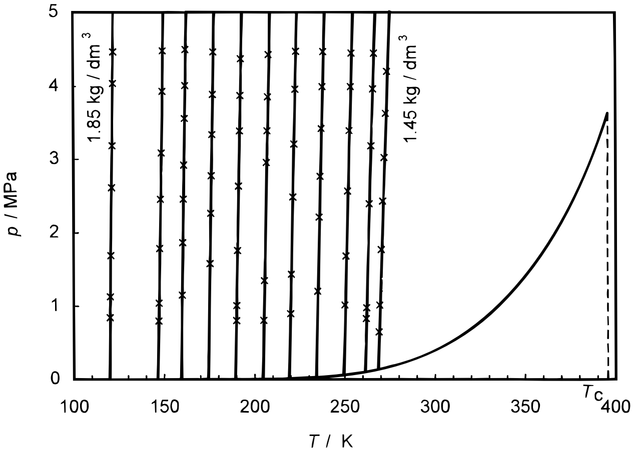

Figure 3. Isochoric measurements on R124 in the liquid-single-phase region.

3. Results

Eleven series of quasi-isochoric measurements were carried out in the single-phase liquid region. The measured values are represented in Figure 3 in the form of a pT diagram. In addition, the measured values are given in Table 1. The relative uncertainty of density measurement to the 95% confidence level is estimated to be less than 1×10^{-3}.

For consistency tests and comparisons with data from the literature, an empiric correlation equation with 11 fittable coefficients was used; this had already proved its worth in the reproduction of the results obtained with other

Table 1. Experimental Densities of R124 along Isochores in the Density Range 1.45 kg/dm^3 < ρ < 1.85 kg/dm^3

ρ/kg dm^{-3}	T_{90}/K	p/MPa	ρ/kg dm^{-3}	T_{90}/K	p/MPa
1.84891	120.025	0.844162	1.62974	206.933	2.95673
1.84872	120.196	1.13125	1.62951	207.303	3.39085
1.84840	120.510	1.69251	1.62925	207.710	3.85828
1.84784	121.032	2.61614	1.62895	208.199	4.42857
1.84750	121.380	3.18663	1.59250	220.003	0.899344
1.84706	121.837	4.03964	1.59220	220.514	1.43981
1.84683	122.092	4.46612	1.59158	221.520	2.48860
1.78124	147.024	0.797866	1.59117	222.203	3.20721
1.78109	147.202	1.04189	1.59075	222.919	3.96158
1.78065	147.710	1.78786	1.59047	223.404	4.47215
1.78027	148.207	2.45775	1.55223	235.060	1.20557
1.77992	148.700	3.08515	1.55162	236.130	2.21454
1.77947	149.212	3.93295	1.55129	236.711	2.76820
1.77917	149.542	4.47870	1.55090	237.402	3.42306
1.74836	160.034	1.15050	1.55057	238.006	3.99569
1.74795	160.508	1.86711	1.55031	238.501	4.46886
1.74762	160.898	2.45967	1.50934	250.212	1.01562
1.74736	161.197	2.91981	1.50890	251.002	1.68695
1.74699	161.615	3.56124	1.50836	252.026	2.56859
1.74674	161.918	4.01198	1.50787	252.999	3.39253
1.74648	162.230	4.49535	1.50752	253.705	3.99643
1.70967	175.504	1.58439	1.50726	254.231	4.44719
1.70929	176.014	2.26546	1.47209	262.013	0.831352
1.70898	176.395	2.77687	1.47197	262.209	0.979173
1.70867	176.797	3.33824	1.47115	264.001	2.39456
1.70836	177.201	3.89133	1.47068	265.005	3.18266
1.70806	177.606	4.46403	1.47022	266.002	3.96747
1.67076	190.059	0.802409	1.46995	266.610	4.44696
1.67064	190.219	1.00794	1.45029	269.006	0.650493
1.67022	190.811	1.76114	1.45006	269.495	1.01436
1.66971	191.510	2.63595	1.44962	270.513	1.77428
1.66928	192.122	3.38853	1.44923	271.397	2.43101
1.66901	192.508	3.87660	1.44887	272.198	3.02442
1.66874	192.898	4.37228	1.44851	273.017	3.63363
1.63103	205.027	0.806495	1.44818	273.780	4.20183
1.63072	205.505	1.35181			

Table 2. Coefficients of the Extended Benedict–Webb–Rubin Equation for the Single-Phase Liquid Region[a]

$d_1 = 5916.3691442$
$d_2 = -3127.4145942$
$d_3 = 1046.2113080$
$d_4 = -900.30786531$
$d_5 = 308.93341055$
$d_6 = -39.197040667$
$d_7 = -10859.250622$
$d_8 = 4778.4728303$
$d_9 = 4948.4892805$
$d_{10} = -1748.3335648$
$D = -251.95864849$

[a] The units used in eq 3 are temperature in kelvins, pressure in MPa, and density in kg dm^{-3}.

refrigerants (Blanke and Weiss, 1992). The correlation equation

$$p = A(T)\rho^2 + B(T)\rho^3 + C(T)\rho^4 + D\rho^6 \tag{3}$$

is valid in the range 120 K < T < 275 K, 1.45 kg/dm^3 < ρ < 1.85 kg/dm^3. $A(T)$, $B(T)$, and $C(T)$ are series expansions in temperature:

$$A(T) = d_1 + d_2(T/T_0) + d_3(T/T_0)^{-1} + d_4(T/T_0)^{-2} + d_5(T/T_0)^{-3} + d_6(T/T_0)^{-4} \tag{3a}$$

$$B(T) = d_7 + d_8(T/T_0) \tag{3b}$$

$$C(T) = d_9 + d_{10}(T/T_0) \tag{3c}$$

D is independent of temperature and $T_0 = 273.15$ K. All coefficients are given in Table 2. The relative density deviations of the measured data, the NIST reference data (Gallagher et al., 1993), and a fundamental equation recently given by de Vries et al. (in press) from eq 3 are shown in Figure 4.

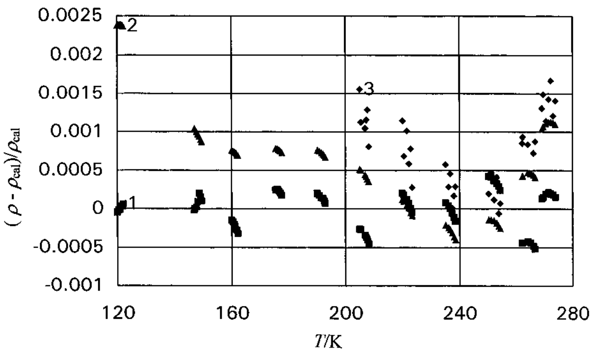

Figure 4. Relative density deviation $(\rho - \rho_{cal})/\rho_{cal}$ in the liquid single-phase region as a function of temperature T. ρ_{cal} is calculated from eq 3. ρ is taken from (1) these measurements, (2) de Vries et al. (in press), and (3) Gallagher et al. (1993).

Table 3. Saturation Properties as Functions of Temperature (ITS-90)

T/K	p/MPa	T/K	ρ'/kg dm^{-3}	ρ''/kg dm^{-3}
119.970	0.000002	119.540	1.84938	
129.937	0.000007			
139.942	0.000007			
149.935	0.000013	146.436	1.78171	
159.985	0.000057	159.273	1.74901	
169.961	0.000205	174.281	1.71061	
185.011	0.000837			
190.081	0.001293	189.433	1.67120	
201.993	0.003486	204.312	1.63150	
207.012	0.005042			
211.995	0.007179			
215.001	0.008801	219.157	1.59301	
229.987	0.022151	233.807	1.55292	
242.019	0.042047			
251.042	0.064860	249.092	1.50990	
256.006	0.081079			
260.033	0.096379			
261.016	0.10052	261.084	1.47251	
266.024	0.12334			
270.006	0.14430	268.315	1.45059	
273.005	0.16184			
293.192	0.32698	293.192	1.37282	0.02025
303.139	0.44472	303.139	1.33866	0.02734
313.098	0.59219	313.098	1.30261	0.03631
323.064	0.77358	323.064	1.26426	0.04763
333.141	0.99611	333.141	1.22260	0.06204
343.151	1.26143	343.151	1.17749	0.08018
353.124	1.57501	353.124	1.12756	0.10324
363.107	1.94374	363.107	1.07045	0.13338
373.099	2.37580	373.099	1.00197	0.17485
383.070	2.87756	383.070	0.91222	0.23701
388.104	3.16257	388.104		0.28585
393.089	3.46810	393.089		0.37407
395.114	3.60167	395.114		0.42756

The vapor pressure values measured in the temperature range between 120 K and 273 K are given in Table 3. In this temperature range, the saturation density in the liquid state was obtained by extrapolating the quasi-isochores to the vapor-pressure curve. These saturated density data are also listed in Table 3. In addition, in this table, the experimental p, ρ', ρ'', and T values obtained with the apparatus based on Archimedes' principle are given. The vapor pressures and the saturated liquid densities are arithmetic mean values. The vapor density in Table 3 was obtained for each vapor pressure with the aid of eq 2 with $d = 0$ and the Gaussian least squares method.

The estimated measurement uncertainties (ISO, 1993) of p, ρ', and ρ'' for temperatures above 290 K with dependence on the temperature are shown in Figure 5. A contribution by the extrapolation according to eq 2 is included.

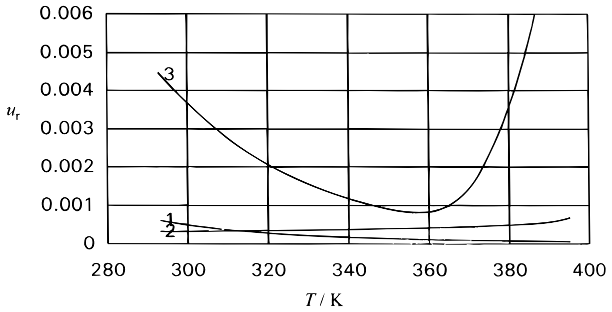

Figure 5. Variation of the relative measurement uncertainty u_r (confidence level: 95%) of (1) the vapor pressure, (2) the saturated liquid density, and (3) the saturated vapor density as a function of temperature T.

Table 4. Simple Equations for the Vapor Pressure and the Saturated Liquid and Vapor Densities

vapor pressure (190 K to 395 K):

$$p/p_c = \exp\{(T_c/T)\sum_{i=1}^{5} a_i[1 - (T/T_c)]^{\lambda_i}\} \qquad (5)$$

AAD = 0.10%, BIAS = 0.03%, SDV = 0.15%, RMS = 0.15%

saturated liquid density (120 K to 383 K):

$$\rho'/\rho_c = 1 + \sum_{i=1}^{4} b_i[1 - (T/T_c)]^{\mu_i} \qquad (6)$$

AAD = 0.03%, BIAS = 0.00%, SDV = 0.04%, RMS = 0.04%

saturated vapor density (293 K to 395 K):

$$\ln(\rho''/\rho_c) = \sum_{i=1}^{7} c_i[1 - (T/T_c)]^{\nu_i} \qquad (7)$$

AAD = 0.02%, BIAS = 0.00%, SDV = 0.03%, RMS = 0.03%

i	λ_i	μ_i	ν_i	a_i	b_i	c_i
1	0.5	1/3	0.2	0.021188665	1.4658391	−253.51947
2	1.0	2/3	0.3	−7.5658435	2.3939923	1133.6252
3	1.5	1	0.5	2.0209171	−3.0327325	−7958.8459
4	2.5	4/3	0.6	−2.9706822	1.9929852	16008.748
5	6.0		0.7	−4.0372700		−10493.090
6			1.0			2049.7131
7			1.3			−509.72391

$T_c = 395.65$ K, $p_c = 3634$ kPa, $\rho_c = 560$ kg/m^3

All the saturation properties listed in Table 3 were fitted to simple equations given in Table 4. The meaning of the abbreviations is

$$\mathrm{AAD} = (1/n)\sum|\Delta x_i| \qquad \text{(absolute average deviation)} \qquad (4a)$$

$$\mathrm{BIAS} = (1/n)\sum\Delta x_i \qquad \text{(bias)} \qquad (4b)$$

$$\mathrm{SDV} = [(1/(n-1))\sum(\Delta x_i - \mathrm{BIAS})^2]^{1/2} \qquad \text{(standard deviation)} \qquad (4c)$$

$$\mathrm{RMS} = [(1/n)\sum\Delta x_i^{\,2}]^{1/2} \qquad \text{(root-mean-square deviation)} \qquad (4d)$$

with

$$\Delta x_i = (x_i - x_{i,\mathrm{calc}})/x_i \qquad (4e)$$

for any physical property x. The critical parameters used were taken from a survey paper presented by McLinden (1990).

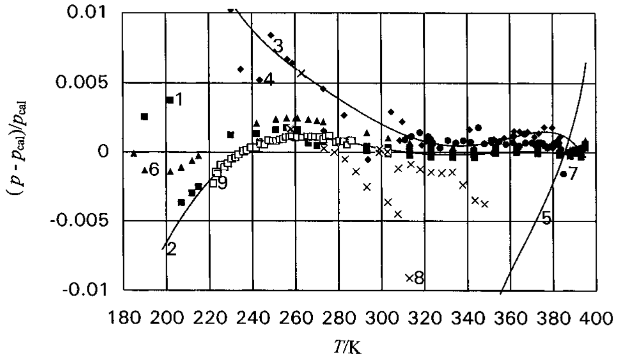

Figure 6. Relative deviation of vapor pressure literature data from values calculated from eq 5 with dependence on temperature T. $(p - p_{\mathrm{cal}})/p_{\mathrm{cal}}$ for (1) this paper, (2) Boyes and Weber (1995), (3) McLinden (1990), (4) Shankland et al. (1990), (5) Kubota et al. (1988), (6) de Vries et al. (in press), (7) Niesen et al. (1994), (8) Baroncini et al. (1991), and (9) Weber and Silva (1994).

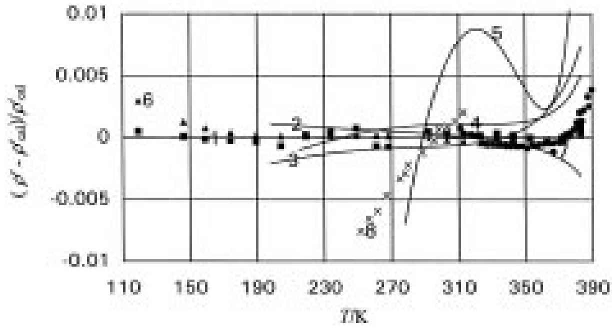

Figure 7. Deviations of the saturated liquid densities from eq 6. $(\rho' - \rho'_{\mathrm{cal}})/\rho'_{\mathrm{cal}}$ for (1) this paper, (2) Gallagher et al. (1993), (3) McLinden (1990), (4) Shankland et al. (1990), (5) Kubota et al. (1988), (6) de Vries et al. (in press), (7) Niesen et al. (1994), and (8) Ripple and Matar (1993).

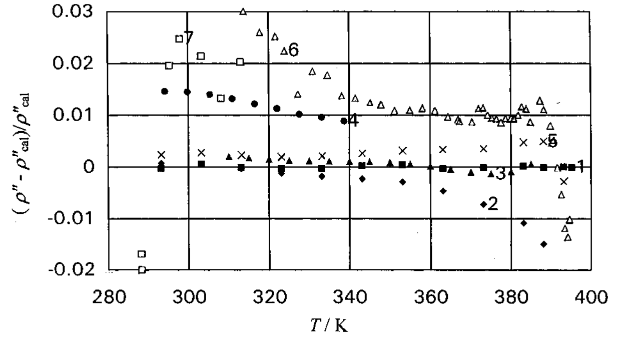

Figure 8. Relative deviation $(\rho'' - \rho''_{\mathrm{cal}})/\rho''_{\mathrm{cal}}$ of the saturated vapor densities. ρ''_{cal} is calculated from eq 7. Key: (1) this paper, (2) Gallagher et al. (1993), (3) Boyes and Weber (1995), (4) Shankland et al. (1990), (5) de Vries et al. (in press), (6) Niesen et al. (1994), and (7) Ripple and Matar (1993).

The relative deviations of the vapor pressure measured by different research groups (Baroncini et al., 1991; Boyes and Weber, 1995; de Vries et al., in press; Kubota et al., 1988; McLinden, 1990; Niesen et al., 1994; Shankland et al., 1990; Weber and Silva, 1994) from eq 5 are plotted in Figure 6. The relative agreement with the values of Boyes and Weber (1995) is better than 3 × 10^{-4}.

Figure 7 is a plot of the relative deviations of the saturated liquid density from eq 6. As mentioned above, eq 6 is valid for temperatures not exceeding 383 K. The agreement with the NIST REFPROP database (Gallagher et al., 1993) in the "extended corresponding states (ECS) model" mode at temperatures below 370 K is better than $2 \times 10^{-3}\rho'$. The relative differences between the measured data and the saturated liquid density calculated for corresponding temperatures $T > 150$ K using the fundamental equation (de Vries et al., in press) do not exceed 1×10^{-3}.

In addition, the relative deviations of values given by McLinden (1990), Niesen et al. (1994), Ripple and Matar (1993), and Kubota et al. (1988) from eq 6 are plotted.

The temperature dependence of $(\rho'' - \rho''_{\mathrm{calc}})/\rho''_{\mathrm{calc}}$ with ρ''_{calc} obtained from eq 7 is shown in Figure 8. For temperatures lower than 395 K, the differences between the saturated vapor densities and the data calculated from the fundamental equation (de Vries et al., in press) show a systematic difference smaller than $5 \times 10^{-3}\rho''$. The maximum deviation from the values given by Boyes and Weber (1995) is only $2 \times 10^{-3}\rho''$. The agreement with REFPROP (Gallagher et al., 1993) in the ECS mode is better than $1.5 \times 10^{-2}\rho''$. The relative differences of the saturated vapor densities measured by Niesen et al. (1994), Ripple and Matar (1993), and Shankland et al. (1990) from eq 7 are shown in Figure 8, too.

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