Thermodynamic Properties of Simple Molecular Fluids: Tetrafluoromethane and Trifluoromethane

Ramón G. Rubio,*,† John A. Zollweg,‡ Jose M. G. Palanco,† Jorge C. G. Calado,§ Jay Miller,‡ and William B. Streett‡

Departamento Química Física, Facultad Químicas, Universidad Complutense, 28040 Madrid, Spain, Complexo I, Istituto Superior Técnico, 1096 Lisboa, Portugal, and School of Chemical Engineering, Cornell University, Ithaca, New York 14853

The thermodynamic properties of CF_4 and CHF_3 have been calculated from an equation of state of the Strobridge type, fitted to extensive $p-V-T$ data sets recently published. The thermodynamic properties under saturation conditions have been compared with previously published data, the agreement being satisfactory except in the near-critical region. The results have been used to discuss the performance of a monatomic fluid model, which is shown to be unsatisfactory.

Introduction

The halocarbon refrigerants are of obvious industrial importance, and also a class of substances of great theoretical interest. Current theories of liquid state highlight the importance of the shape of the molecule and of its polarity. The halomethane refrigerants are all based on a quasi-spherical nonpolar molecule—methane itself—and so can be regarded as a series of case studies showing the effect of increasing shape anisotropy and increasing polarity by the simple substitution of fluorine and/or chlorine for hydrogen atoms. As already pointed out (*1-3*), it is difficult to appreciate the overall effect of these substitutions without a correlation of the available experimental data, and such correlations, whether in the form of tables or equations, are essential to industrial designers and operators.

Two of the simplest halomethanes are CF_4 and CHF_3. While their grosser features may be modeled by quasi-spherical molecules, the large differences of the behavior of the $CF_4 + CHF_3$ mixture with respect to that of the ideal mixture are symptomatic of the anisotropies inherent in their microscopic interactions (*4*, *5*). Rubio et al. (*3*, *6*) have pointed out that a large number of papers in the literature arrive at contradictory conclusions concerning the intermolecular potential model for these two molecules. One can expect the anisotropies of the potential to be dependent on the packing of the molecules, i.e. the density (especially those arising from the shape of the molecules), and since this can be tuned by varying the temperature and the pressure, the availability of thermodynamic properties in wide ranges of p and T will be helpful in clarifying the main characteristics of the intermolecular potential of these simple molecular fluids, a necessary step in our ability to predict their thermodynamic properties.

Stewart et al. (*7*) summarized the available thermodynamic data for many halocarbons and showed that most of the results are concentrated in the low-density region. Recently, extensive experimental studies of the $p-V-T$ surfaces of CF_4 (*3*) and CHF_3 (*6*) have been published. Although most of our measurements were obtained in the high-density region, there is a significant overlap with most of the previous low-density studies. Figures 1 and 2 show the $p-T$ ranges for which density data are available.

In this paper we report calculated thermodynamic properties of CF_4 in the ranges $90 < T/K < 420$ and $0 < p/bar < 1000$ and of CHF_3 in the ranges $126 < T/K < 332$ and $0 < p/bar < 1000$, derived from an equation of state of the Strobridge type fitted to the experimental $p-V-T$ data.

Equation of State

For describing and interpolating the existing data we have used the Strobridge equation (*8*)

$$p = RT\rho + (A_1RT + A_2 + A_3/T + A_4/T^2 + A_5/T^4)\rho^2 + (A_6RT + A_7)\rho^3 + A_8T\rho^4 + (A_9/T^2 + A_{10}/T^3 + A_{11}/T^4)\rho^3 \exp(A_{16}\rho^2) + (A_{12}/T^2 + A_{13}/T^3 + A_{14}/T^4)\rho^5 \exp(A_{16}\rho^2) + A_{15}\rho^6 \quad (1)$$

Detailed discussions of the data used to obtain the A_i parameters of eq 1 and of the differences between experimental and calculated results have been included in previous papers (*3*, *6*). Table I gives the values of the A_i ($I = 1-16$) constants for both fluids, as well as their estimated uncertainties and the variances of the fits. Even though, for the high-density data, each isotherm can be fitted with mean square deviations (msd) of 0.01% in the density, the overall fit leads to an msd of 0.1% for both CF_4 and CHF_3. These results are similar to those found by Calado et al. (*2*) for ethylene. The increase of the msd is mainly due to the existence of some inconsistencies between the data obtained by different authors (*3*, *6*).

Thermodynamic Properties of CF_4

Information about the coexistence curve of the fluids is necessary to calculate the thermodynamic properties. Lobo and Staveley (*9*) have discussed in detail the orthobaric properties of CF_4, and we have used the vapor pressure curve proposed by them. The thermodynamic properties of the gas and saturated liquid were calculated by using standard thermodynamic formulas. Contrary to ref 2, we have used eq 1 for the gas phase instead of the virial equation of state. Table II shows the properties along the saturation curve for CF_4. The saturated densities agree with those of Lobo and Staveley within 0.2% below 190 K, but the disagreement increases above that temperature, reaching about 2% at 220 K. It should be pointed out that the liquid densities reported by Lobo and Staveley are those of Terry et al. (*19*). The main source of discrepancy is the fact that the orthobaric vapor density ρ_v of Lobo and Staveley was calculated from the virial equation of state up to the third coefficient, while we have used eq 1; the difference in ρ_v at 200 K is 3%. Using our value for ρ_v and the law of rectilinear diameters obtained with the values reported in ref 9 for $T < 180$ K, we have found that the differences from our results decrease to less than 0.4%. McCormack and Schneider (*11*) have claimed that the fourth virial coefficient is necessary in order to explain their $p-V-T$ data in the ranges $T < 750$ K and $p < 50$ bar. Kratzke et al. (*12*) have discussed

* To whom correspondence should be addressed.
† Universidad Complutense.
‡ Cornell University.
§ Instituto Superior Técnico.

0021-9568/91/1736-0171$02.50/0

Table I. Coefficients A_i (i = 1-16), Their Estimated Errors, and Their Estimated Variance of Fit for Equation 1 for CF_4 and CHF_3

substance CF_4		substance CHF_3	
i	A_i	i	A_i
1	0.041 ± 0.001 dm^3 mol^{-1}	1	0.045457 ± 0.003 dm^3 mol^{-1}
2	1.76 ± 0.04 bar dm^6 mol^{-2}	2	6.9009 ± 0.07 bar dm^6 mol^{-2}
3	−1947 ± 3 bar dm^6 K mol^{-2}	3	−5684.3 ± 2 bar dm^6 K mol^{-2}
4	(1.347 ± 0.002) × 10^5 bar dm^6 K^2 mol^{-2}	4	(5.8935 ± 0.01) × 10^5 bar dm^6 K^2 mol^{-2}
5	(4.835 ± 0.005) × 10^8 bar dm^6 K^4 mol^{-2}	5	−(2.6234 ± 0.009) × 10^9 bar dm^6 K^4 mol^{-2}
6	(0.53 ± 0.02) × 10^{-2} dm^6 mol^{-2}	6	−(6.9026 ± 0.5) × 10^{-3} dm^6 mol^{-2}
7	−0.337 ± 0.004 bar dm^9 mol^{-3}	7	−0.21356 ± 0.007 bar dm^9 mol^{-3}
8	(4.00 ± 0.05) × 10^{-5} bar dm^{12} K^{-1} mol^{-4}	8	(2.2642 ± 0.1) × 10^{-5} bar dm^{12} K^{-1} mol^{-4}
9	(5846 ± 5) × 10 bar dm^9 K^2 mol^{-3}	9	−33930 ± 80 bar dm^9 K^2 mol^{-3}
10	−(1.102 ± 1) × 10^7 bar dm^9 K^3 mol^{-3}	10	(2.9711 ± 0.004) × 10^7 bar dm^9 K^3 mol^{-3}
11	(6.556 ± 0.007) × 10^8 bar dm^9 K^4 mol^{-3}	11	−(3.4292 ± 0.009) × 10^9 bar dm^9 K^4 mol^{-3}
12	−28.6 ± 0.4 bar dm^{15} K^2 mol^{-5}	12	47.361 ± 0.3 bar dm^{15} K^2 mol^{-5}
13	7970 ± 14 bar dm^{15} K^3 mol^{-5}	13	−64699 ± 2 bar dm^{15} K^3 mol^{-5}
14	−(1.2011 ± 0.0004) × 10^6 bar dm^{15} K^4 mol^{-5}	14	(7.8646 ± 0.008) × 10^6 bar dm^{15} K^4 mol^{-5}
15	(4.749 ± 0.002) × 10^{-5} bar dm^{18} mol^{-6}	15	(2.0224 ± 0.007) × 10^{-5} bar dm^{18} mol^{-6}
16	−0.0040 ± 0.001 dm^6 mol^{-2}	16	−0.0040 ± 0.001 dm^6 mol^{-2}
	estimated variance of fit = 15		estimated variance of fit = 23

Table II. Thermodynamic Properties of Tetrafluoromethane along the Saturation Curve

T/K	P/bar	ρ_l/(mol dm^{-3})	ρ_v/(mol dm^{-3})	ΔH_v/(kJ mol^{-1})	$-E_\sigma$/(kJ mol^{-1})	$-S_\sigma$/(J mol^{-1} K^{-1})
95	0.0032	21.067	4.0×10^{-4}	14.038	13.246	57.378
100	0.0076	20.817	9.2×10^{-4}	13.799	12.965	54.594
110	0.0338	20.288	3.69×10^{-3}	13.360	12.440	49.799
120	0.1122	19.732	1.128×10^{-2}	12.957	11.952	45.778
130	0.3020	19.163	2.817×10^{-2}	12.566	11.483	42.270
140	0.6925	18.571	6.060×10^{-2}	12.162	11.017	39.079
150	1.4027	17.955	0.1165	11.721	10.541	36.074
160	2.5775	17.309	0.2058	11.221	10.046	33.182
170	4.3827	16.623	0.3410	10.642	9.527	30.365
180	7.0010	15.881	0.5389	9.968	8.979	27.604
190	10.6300	15.063	0.8236	9.169	8.396	24.880
200	15.4857	14.129	1.2340	8.205	7.768	22.161
210	21.8122	12.998	1.8414	7.003	7.067	19.378
215	25.6170	12.301	2.2618	6.268	6.670	17.922
220	29.9096	11.431	2.8056	5.391	6.219	16.378
225	34.7538	10.087	3.5426	4.246	5.636	14.627

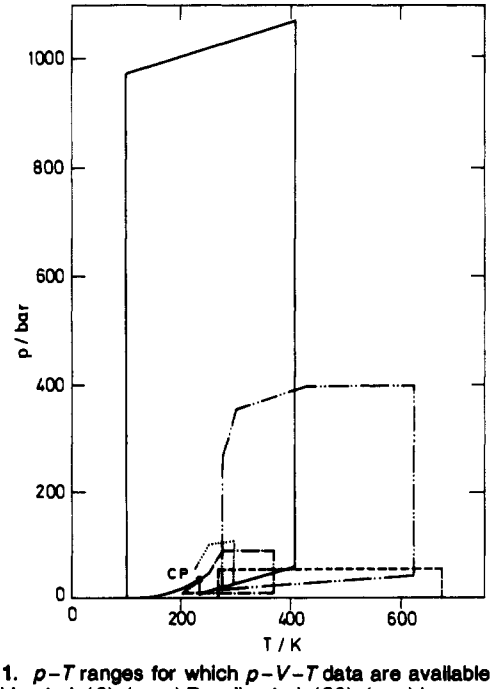

Figure 1. $p-T$ ranges for which $p-V-T$ data are available for CF_4: (—) Rubio et al. (*2*); (-••-) Douslin et al. (*30*); (-•-) Lange and Stein (*31*); (•••) Martin and Bhada (*32*); (--) McCormack and Schneider (*11*).

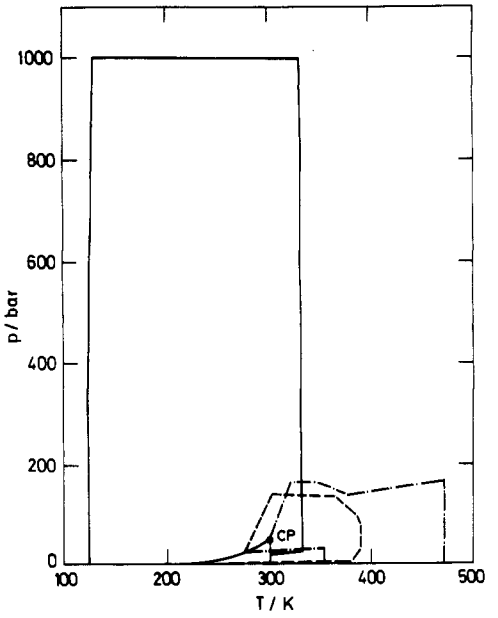

Figure 2. $p-T$ ranges for which $p-V-T$ data are available for CHF_3: (—) Rubio et al. (*6*); (--) Hou and Martin (*17*); (-•-) Belzile et al. (*33*) and Hori et al. (*16*).

in detail the errors arising in the thermodynamic properties from an insufficient knowledge of the virial coefficients. Figure 3 shows the data from different sources.

As a further test of the equation of state, we have calculated the second virial coefficients from extrapolation of $B = (Z - 1)/\rho$ to $\rho \rightarrow 0$, where Z is the compressibility factor. Figure 4 shows the results, together with the values recommended by

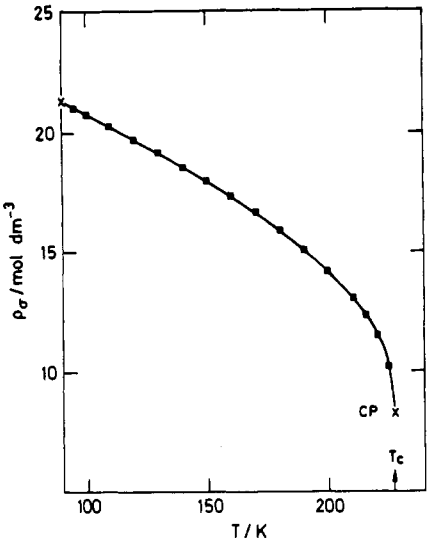

Figure 3. Orthobaric densities for CF_4 according to different sources: (—) Lobo and Staveley (*9*); (■) Rubio et al. (*3*); (×) CP, critical point.

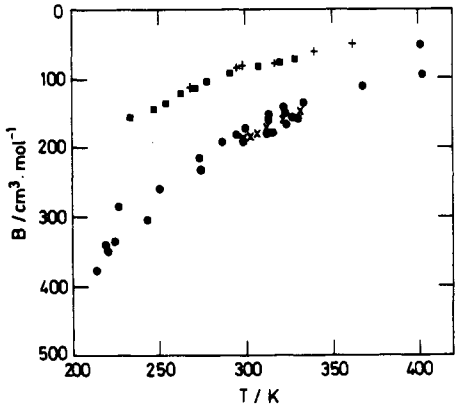

Figure 4. Second virial coefficients obtained from the proposed equation of state for CHF_3 (×) and those recommended by Dymond and Smith (*20*) (○). For CF_4, + are the values from eq 1 and ■ are the values from Dymond and Smith.

Dymond and Smith (*20*). The agreement is very good.

We have calculated the heat of vaporization from

$$\Delta H_v = T\left(\frac{\partial p}{\partial T}\right)_\sigma \left(\frac{1}{\rho_v} - \frac{1}{\rho_l}\right) \qquad (2)$$

where the subscript σ refers to orthobaric conditions. The disagreement with the values of Lobo and Staveley is less than 2% except at 220 K, where it is of the order of 6%. On the other hand, the difference from the value reported by Smith and Pace (*13*) at the normal boiling point is 1.5%. Since we have used the same vapor pressure as Lobo and Staveley (*9*), the differences in ΔH_v clearly arise from the calculated orthobaric densities.

Table III shows the mechanical coefficients of liquid CF_4 under saturation conditions. Besides eq 1 and the vapor pressure equation of Lobo and Staveley, the speed of sound data of Baglol et al. (*14*) and the heat capacity results of Smith and Pace (*13*) have been used. For the thermodynamic relations involved in the calculations, we refer the reader to the paper of Lobo and Staveley (*9*). Once again, the small differences between the results of Table III and those of ref 9 show the results of the thermodynamic properties of CF_4 at round values of p and T. Tables IV–IX show the thermodynamic properties at selected values of p and T.

Table III. Mechanical Coefficients of Liquid Tetrafluoromethane under Saturation Conditions

T/K	$\beta \times 10^4$/bar^{-1}	$\alpha \times 10^3$/K^{-1}	γ/ (bar K^{-1})	γ_σ/ (bar K^{-1})	$\alpha_\sigma \times 10^3$/K^{-1}
95	0.85	2.32	27.13	0.00	2.32
100	0.92	2.46	26.82	0.00	2.46
110	1.09	2.67	24.62	0.00	2.67
120	1.31	2.85	21.76	0.01	2.85
130	1.61	3.04	18.92	0.03	3.04
140	2.00	3.26	16.31	0.05	3.25
150	2.52	3.53	13.98	0.09	3.51
160	3.26	3.89	11.92	0.15	3.84
170	4.34	4.37	10.08	0.22	4.28
180	6.00	5.07	8.44	0.31	4.88
190	8.82	6.13	6.95	0.42	5.76
200	14.27	7.96	5.58	0.55	7.17
210	27.56	11.82	4.29	0.72	9.85
215	43.75	15.96	3.65	0.81	12.43
220	85.00	25.38	2.99	0.91	17.63

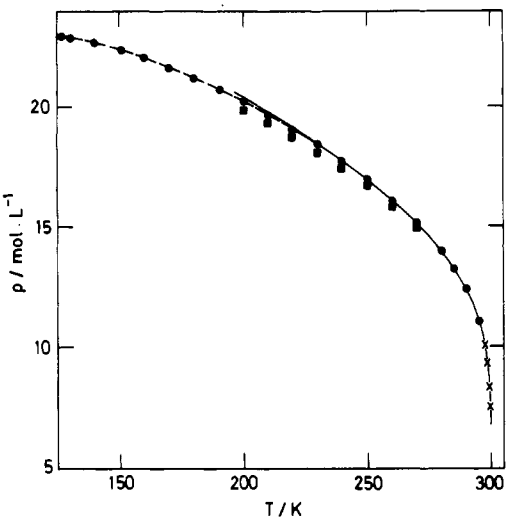

Figure 5. Orthobaric densities for CHF_3 according to different sources: (—) equation of Hori et al. (*16*); (×) near-critical data of ref 16; (●) data of Rubio et al. (*6*); (■) data of Kondo et al. (*19*).

Thermodynamic Properties of CHF_3

For CHF_3 the vapor pressures reported by Valentine et al. (*15*), Hori et al. (*16*), and Hou and Martin (*17*) were fitted to an equation like that proposed by Goodwin (*18*). Table X shows the thermodynamic properties of CHF_3 under saturation conditions at selected values of T, and Table XI shows the mechanical coefficients at the same conditions. Figure 5 shows the saturation density for the liquid, as well as the values reported by Kondo et al. (*19*) and the near-critical data of Hori et al. (*16*). It can be observed that the agreement with the most recent equation of state of Hori et al. (*16*) is excellent, with discrepancies starting to appear near the lower limit of applicability of Hori's equation (203 K). Our results extrapolate very smoothly to the near-critical experimental data (*16*). The heat of vaporization at 190.97 K measured by Valentine et al. (*15*) is 1% lower than that reported in Table II; no other ΔH_v data have been found.

Figure 4 shows the second virial coefficients of CHF_3 calculated as described above for CF_4. As it can be observed, the results follow the general trend of the very scattered available data (*20*). Tables XII–XVII show the thermodynamic properties at selected values of p and T.

Monatomic Fluid Model

As already mentioned, there exists a strong controversy about the intermolecular potential model suitable for simple molecular fluids such as the ones discussed in this paper. While

Table IV. Density (mol dm^{-3}) of Tetrafluoromethane at Round Values of Pressure (P, bar) and Temperature (T, K)

	density															
T	P = 5	P = 10	P = 15	P = 25	P = 50	P = 100	P = 200	P = 300	P = 400	P = 500	P = 600	P = 700	P = 800	P = 900	P = 1000	P = 1100
95	21.076	21.085	21.094	21.111	21.155	21.238	21.395									
100	20.826	20.836	20.845	20.864	20.910	20.998	21.164	21.318	21.460							
110	20.299	20.310	20.321	20.343	20.395	20.497	20.686	20.859	21.019	21.169	21.310	21.442	21.569	21.689	21.803	21.913
120	19.748	10.761	19.774	19.779	19.860	19.978	20.195	20.392	20.573	20.741	20.897	21.045	21.184	21.316	21.441	21.562
130	19.178	19.193	19.208	19.238	19.311	19.448	19.699	19.923	20.127	20.315	20.489	20.651	20.804	20.948	21.085	21.216
140	18.587	18.606	18.624	18.659	18.746	18.908	19.199	19.454	19.684	19.893	20.085	20.264	20.431	20.588	20.736	20.877
150	17.972	17.994	18.016	18.059	18.164	18.356	18.694	18.985	19.243	19.475	19.687	19.883	20.064	20.234	20.394	20.546
160	17.323	17.350	17.378	17.431	17.559	17.790	18.184	18.516	18.805	19.062	19.295	19.508	19.705	19.888	20.060	20.222
170	16.627	16.663	16.697	16.765	16.923	17.204	17.667	18.046	18.369	18.654	18.908	19.139	19.352	19.549	19.732	19.905
180		15.910	15.956	16.044	16.247	16.594	17.142	17.574	17.935	18.249	18.526	18.777	19.005	19.216	19.411	19.594
190			15.120	15.243	15.514	15.953	16.605	17.099	17.503	17.847	18.149	18.419	18.664	18.888	19.096	19.290
200				14.308	14.696	15.270	16.056	16.621	17.071	17.449	17.776	18.067	18.328	18.567	18.787	18.991
210				13.107	13.744	14.533	15.493	16.140	16.641	17.054	17.408	17.719	17.998	18.251	18.483	18.698
220					12.542	13.725	14.913	15.655	16.211	16.662	17.044	17.377	17.673	17.941	18.185	18.411
240	0.261	0.545	0.858	1.605	5.719	11.787	13.702	14.676	15.356	15.888	16.328	16.706	17.038	17.335	17.604	17.858
250	0.249	0.517	0.808	1.478	4.184	10.605	13.073	14.183	14.932	15.507	15.978	16.378	16.728	17.040	17.322	17.579
260	0.238	0.492	0.764	1.375	3.530	9.319	12.432	13.691	14.512	15.131	15.632	16.056	16.424	16.750	17.044	17.312
270	0.229	0.470	0.726	1.290	3.123	8.091	11.788	13.201	14.096	14.760	15.292	15.739	16.125	16.466	16.772	17.050
280	0.220	0.450	0.692	1.217	2.833	7.072	11.149	12.717	13.686	14.395	14.958	15.427	15.831	16.186	16.504	16.793
290	0.212	0.432	0.662	1.154	2.610	6.279	10.527	12.242	13.283	14.036	14.630	15.121	15.543	15.912	16.242	16.540
300	0.204	0.415	0.635	1.099	2.432	5.665	9.932	11.778	12.889	13.685	14.308	14.822	15.260	15.644	15.985	16.293
310	0.197	0.400	0.610	1.050	2.284	5.181	9.373	11.329	12.505	13.342	13.994	14.529	14.984	15.381	15.733	16.051
320	0.190	0.386	0.587	1.006	2.158	4.791	8.855	10.897	12.132	13.008	13.687	14.242	14.713	15.123	15.486	15.813
330	0.184	0.373	0.566	0.966	2.050	4.469	8.381	10.484	11.771	12.682	13.387	13.962	14.449	14.871	15.245	15.581
340	0.179	0.361	0.547	0.930	1.955	4.199	7.949	10.091	11.423	12.367	13.096	13.689	14.191	14.625	15.009	15.353
350	0.173	0.350	0.529	0.897	1.871	3.968	7.557	9.720	11.088	12.062	12.813	13.424	13.939	14.585	14.778	15.131
360	0.168	0.339	0.513	0.867	1.796	3.768	7.203	9.369	10.767	11.767	12.538	13.165	13.694	14.150	14.553	14.913
370	0.164	0.329	0.497	0.839	1.728	3.592	6.881	9.040	10.460	11.482	12.272	12.914	13.455	13.922	14.333	14.701
380	0.159	0.320	0.483	0.813	1.666	3.437	6.589	8.731	10.167	11.208	12.015	12.670	13.222	13.699	14.118	14.493
390	0.155	0.311	0.469	0.789	1.610	3.298	6.324	8.441	9.888	10.945	11.765	12.434	12.996	13.482	13.909	14.290
400	0.151	0.303	0.456	0.766	1.558	3.173	6.082	8.170	9.622	10.691	11.525	12.204	12.776	13.270	13.704	14.092
410	0.147	0.295	0.444	0.745	1.510	3.060	5.860	7.916	9.369	10.448	11.293	11.982	12.563	13.064	13.505	13.899
420	0.144	0.288	0.433	0.725	1.465	2.956	5.657	7.677	9.129	10.215	11.069	11.767	12.356	12.864	13.312	13.711

Table V. Isothermal Compressibility (10^{-4}/bar) for Tetrafluoromethane at Various Pressures (P, bar) and Temperatures (T, K)

	isothermal compressibility													
T	P = 5	P = 10	P = 15	P = 25	P = 50	P = 100	P = 200	P = 300	P = 400	P = 500	P = 600	P = 700	P = 800	P = 900
95	0.85	0.84	0.84	0.83	0.81	0.77	0.70							
100	0.91	0.91	0.90	0.89	0.87	0.82	0.75	0.69	0.64					
110	1.08	1.07	1.07	1.05	1.02	0.97	0.87	0.80	0.74	0.68	0.64	0.60	0.57	0.54
120	1.30	1.29	1.28	1.26	1.22	1.15	1.02	0.92	0.85	0.78	0.73	0.68	0.64	0.60
130	1.59	1.58	1.57	1.54	1.48	1.37	1.20	1.07	0.97	0.89	0.82	0.76	0.71	0.67
140	1.98	1.96	1.94	1.90	1.81	1.65	1.41	1.24	1.11	1.01	0.92	0.85	0.79	0.74
150	2.50	2.47	2.43	2.37	2.23	2.00	1.67	1.44	1.27	1.14	1.03	0.95	0.88	0.81
160	3.23	3.18	3.12	3.02	2.80	2.45	1.97	1.66	1.44	1.28	1.15	1.05	0.96	0.89
170	4.32	4.22	4.13	3.96	3.58	3.03	2.34	1.93	1.64	1.44	1.28	1.16	1.06	0.97
180		5.89	5.71	5.38	4.71	3.81	2.80	2.23	1.87	1.61	1.42	1.27	1.15	1.05
190			8.46	7.75	6.44	4.88	3.35	2.58	2.12	1.80	1.57	1.39	1.25	1.14
200				12.39	9.33	6.39	4.04	2.99	2.40	2.00	1.73	1.52	1.36	1.23
210				24.99	14.91	8.65	4.89	3.47	2.71	2.23	1.90	1.66	1.47	1.33
220					28.90	12.18	5.96	4.02	3.05	2.47	2.08	1.80	1.59	1.42
240	2083.40	1091.83	768.82	531.86	625.38	28.35	8.97	5.38	3.86	3.02	2.48	2.11	1.84	1.63
250	2071.97	1077.91	751.50	502.70	383.64	46.19	11.01	6.20	4.32	3.32	2.70	2.28	1.97	1.73
260	2062.27	1066.46	737.82	482.28	317.24	71.63	13.47	7.12	4.82	3.64	2.93	2.45	2.10	1.84
270	2053.98	1056.94	726.80	467.19	284.27	94.78	16.30	8.14	5.36	3.98	3.16	2.62	2.24	1.96
280	2046.86	1048.94	717.78	455.62	264.16	107.55	19.41	9.25	5.92	4.33	3.41	2.81	2.38	2.07
290	2040.72	1042.18	710.31	446.50	250.54	112.33	22.65	10.38	6.52	4.70	3.66	2.99	2.53	2.19
300	2035.41	1036.41	704.05	439.15	240.67	113.19	25.81	11.56	7.13	5.08	3.92	3.18	2.68	2.30
310	2030.79	1031.46	698.76	433.13	233.21	112.39	28.74	12.76	7.75	5.46	4.18	3.38	2.82	2.42
320	2026.76	1027.20	694.25	428.13	227.38	110.97	31.34	13.94	8.37	5.85	4.45	3.57	2.97	2.54
330	2023.23	1023.50	690.38	423.93	222.71	109.38	33.56	15.08	8.99	6.23	4.71	3.77	5.12	2.66
340	2020.15	1020.28	687.04	420.37	218.90	107.83	35.42	16.15	9.60	6.62	4.98	5.96	5.27	2.78
350	2017.40	1017.46	684.13	417.32	215.74	106.40	36.94	17.16	10.19	7.00	5.24	4.15	3.42	2.90
360	2014.99	1014.99	681.61	414.70	213.09	105.09	38.19	18.09	10.76	7.37	5.50	4.35	3.57	3.02
370	2012.86	1012.81	679.39	412.43	210.84	103.93	39.19	18.95	11.31	7.73	5.75	4.53	3.72	3.14
380	2010.96	1010.89	677.44	410.45	208.92	102.89	40.00	19.72	11.82	8.08	6.00	4.72	3.86	3.25
390	2009.28	1009.18	675.73	408.72	207.27	101.97	40.65	20.42	12.31	8.41	6.24	4.90	4.00	3.37
400	2007.78	1007.67	674.21	407.20	205.84	101.15	41.18	21.05	12.76	8.73	6.48	5.08	4.14	3.48
410	2006.44	1006.33	672.86	405.86	204.59	100.43	41.60	21.61	13.19	9.04	6.70	5.25	4.28	3.59
420	2005.24	1005.13	671.67	404.67	203.49	99.79	41.95	22.11	13.59	9.33	6.92	5.42	4.41	3.69

site–site potentials seem to be necessary for dealing with noticeable anisotropies of shape (*21*, *22*), surprisingly good results were reported by Huang and O'Connell (*23*) from a correlation based on the assumption of a spherical reference system common to all the fluids, which implies the same intermolecular potential to be valid for all of them. Recently, it has been shown that although bulk modulus data of several molecular fluids seem to support this conclusion (*24*), other properties, such as the residual heat capacity at constant volume, indicate that some characteristics of the intermolecular potential (e.g. the slope of the repulsive branch) differ from fluid to fluid. This conclusion is in agreement with results obtained from application of the Gubbins–Gray perturbation theory (*2*, *3*). In this paper we pursue a little further the study carried out in ref 24, since new information can be obtained from the residual properties reported in this paper.

As previously (*24*), the starting point is the assumption of an effective intermolecular potential of the form

$$U_{eff}(r,T,V) = \frac{A(T,V)}{r^n} - \frac{B(T,V)}{r^m} \qquad (3)$$

Values of n and m for different molecular fluids have been reported by Compostizo et al. (*24*).

Using eq 3 and the virial theorem, Grindley and Lind have concluded that

$$(m - n)(\partial\langle U_a\rangle/\partial V) = (3 + n)p + 3V(\partial p/\partial V) - nT(\partial p/\partial T) \qquad (4)$$

where

$$\langle U_a\rangle = -\frac{N^2}{2V}\int \frac{B(T,V)}{r^m} g(r,T,V)\, d\vec{r} \qquad (5)$$

N/V being the number density. As is obvious from eq 5, $\langle U_a\rangle$ gives a measure of the contribution of the attractive forces to the total energy of the fluid. Figure 6 shows $(\partial\langle U_a\rangle/\partial V)_T$ calculated from eq 4 for CF_4 and for CCl_4 along the saturation curve. We have used n = 19 for CF_4, n = 22 for CCl_4 (*24*) and m = 6 in both cases. As shown by Grindley and Lind (*25*), eq 4 implies that $(\partial\langle U_a\rangle/\partial V)_T$ should be temperature-independent along an isochore, whereas Figure 6 shows a clear temperature dependence, which indicates that eq 3 is not good enough for simple molecular fluids like CF_4. Similar conclusions hold when the results of CHF_3 are analyzed.

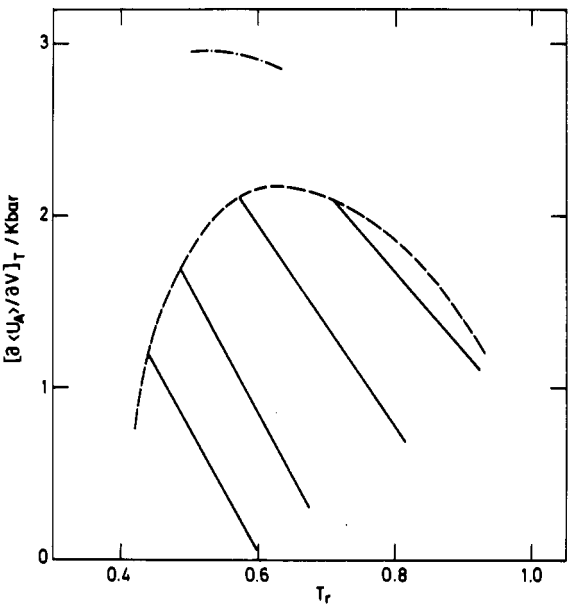

Figure 6. Density derivative of the mean attractive energy vs reduced temperature ($T_r = kT/\epsilon$) for CF_4 and CCl_4: (--) CF_4 at the saturation curve; (—) CF_4 isochores; (–·–) CCl_4 at the saturation curve.

Table VI. Thermal Expansion Coefficient (10^{-3} K^{-1}) for Tetrafluoromethane at Various Pressures (P, bar) and Temperatures (T, K)

	thermal expansion coefficient															
T	$P = 5$	$P = 10$	$P = 15$	$P = 25$	$P = 50$	$P = 100$	$P = 200$	$P = 300$	$P = 400$	$P = 500$	$P = 600$	$P = 700$	$P = 800$	$P = 900$	$P = 1000$	$P = 1100$
95	2.31	2.30	2.30	2.29	2.26	2.21	2.12									
100	2.45	2.45	2.44	2.43	2.39	2.33	2.22	2.12	2.03							
110	2.66	2.65	2.64	2.63	2.58	2.50	2.35	2.23	2.12	2.02	1.94	1.86	1.79	1.73	1.67	1.61
120	2.84	2.83	2.82	2.79	2.73	2.63	2.45	2.30	2.17	2.06	1.97	1.88	1.81	1.74	1.68	1.62
130	3.02	3.01	2.99	2.96	2.88	2.75	2.53	2.35	2.21	2.09	1.98	1.89	1.81	1.74	1.67	1.61
140	3.24	3.22	3.20	3.15	3.06	2.89	2.62	2.41	2.25	2.11	2.00	1.90	1.81	1.73	1.67	1.60
150	3.51	3.48	3.45	3.39	3.26	3.04	2.71	2.47	2.28	2.13	2.01	1.90	1.81	1.73	1.66	1.59
160	3.87	3.82	3.78	3.70	3.52	3.23	2.82	2.54	2.32	2.15	2.02	1.90	1.81	1.72	1.65	1.58
170	4.36	4.30	4.23	4.12	3.86	3.47	2.95	2.61	2.37	2.18	2.03	1.91	1.81	1.72	1.64	1.58
180		5.00	4.90	4.71	4.32	3.76	3.10	2.69	2.42	2.21	2.05	1.92	1.81	1.72	1.64	1.57
190			5.96	5.62	4.96	4.14	3.27	2.78	2.47	2.24	2.07	1.93	1.81	1.72	1.63	1.56
200				7.22	5.94	4.63	3.46	2.88	2.52	2.27	2.08	1.94	1.82	1.72	1.63	1.56
210				11.00	7.62	5.29	3.69	2.99	2.58	2.31	2.10	1.95	1.82	1.72	1.63	1.55
220					11.22	6.21	3.95	3.11	2.65	2.34	2.12	1.96	1.82	1.72	1.63	1.55
240	4.73	5.42	6.29	8.92	51.57	9.38	4.54	3.35	2.77	2.41	2.16	1.98	1.83	1.72	1.62	1.54
250	4.48	5.06	5.75	7.67	21.02	11.80	4.86	3.47	2.83	2.44	2.18	1.99	1.84	1.72	1.62	1.53
260	4.26	4.75	5.31	6.77	14.01	13.85	5.18	3.59	2.88	2.47	2.19	1.99	1.84	1.71	1.61	1.53
270	4.06	4.47	4.94	6.08	10.79	14.06	5.46	3.69	2.93	2.49	2.21	2.00	1.84	1.71	1.61	1.52
280	3.88	4.23	4.62	5.54	8.86	12.73	5.67	3.78	2.97	2.51	2.22	2.00	1.84	1.71	1.60	1.52
290	3.72	4.02	4.35	5.09	7.57	11.06	5.80	3.84	3.00	2.53	2.22	2.00	1.84	1.71	1.60	1.51
300	3.57	3.83	4.11	4.72	6.64	9.56	5.82	3.88	3.02	2.54	2.22	2.00	1.83	1.70	1.59	1.50
310	3.43	3.66	3.89	4.41	5.94	8.34	5.75	3.89	3.03	2.54	2.22	2.00	1.83	1.69	1.58	1.49
320	3.31	3.50	3.71	4.14	5.38	7.36	5.60	3.88	3.03	2.54	2.22	1.99	1.82	1.68	1.58	1.49
330	3.19	3.36	3.54	3.91	4.93	6.57	5.40	3.84	3.01	2.53	2.21	1.98	1.81	1.67	1.57	1.43
340	3.08	3.23	3.38	3.70	4.56	5.93	5.17	3.79	2.99	2.51	2.19	1.97	1.80	1.66	1.55	1.47
350	2.98	3.11	3.25	3.52	4.25	5.40	4.93	3.71	2.96	2.49	2.18	1.95	1.78	1.65	1.54	1.45
360	2.89	3.00	3.12	3.36	3.98	4.96	4.69	3.63	2.91	2.46	2.16	1.94	1.77	1.64	1.53	1.44
370	2.80	2.90	3.01	3.22	3.75	4.59	4.45	3.53	2.87	2.43	2.13	1.92	1.75	1.62	1.52	1.43
380	2.72	2.81	2.90	3.08	3.54	4.27	4.22	3.43	2.81	2.40	2.11	1.90	1.73	1.61	1.50	1.42
390	2.64	2.72	2.80	2.97	3.36	3.99	4.00	3.32	2.76	2.36	2.08	1.87	1.72	1.59	1.49	1.40
400	2.57	2.64	2.71	2.86	3.20	3.75	3.80	3.21	2.69	2.32	2.05	1.85	1.70	1.57	1.47	1.39
410	2.50	2.57	2.63	2.76	3.06	3.54	3.62	3.11	2.63	2.28	2.02	1.83	1.67	1.55	1.45	1.37
420	2.44	2.40	2.55	2.66	2.93	3.35	3.44	3.00	2.57	2.23	1.99	1.80	1.65	1.53	1.44	1.36

Table VII. Thermal Pressure Coefficient (bar/K) for Tetrafluoromethane at Various Pressures (P, bar) and Temperatures (T, K)

	thermal pressure coefficient																	
T	P = 5	P = 10	P = 15	P = 25	P = 50	P = 100	P = 200	P = 300	P = 400	P = 500	P = 600	P = 700	P = 800	P = 900	P = 1000	P = 1100	P = 1000	P = 1100
95	27.21	27.30	27.38	27.55	27.96	28.73	30.11											
100	26.90	26.97	27.05	27.20	27.56	28.24	29.48	30.56	31.53									
110	24.69	24.76	24.82	24.95	25.27	25.86	26.94	27.90	28.75	29.52	30.21	30.84	31.41	31.93	32.41	32.85	1.67	1.61
120	21.82	21.89	21.95	22.07	22.37	22.93	23.96	24.86	25.68	26.41	27.08	27.70	28.26	28.78	29.27	29.72	1.68	1.62
130	18.98	19.04	19.10	19.23	19.52	20.08	21.09	21.99	22.79	23.52	24.19	24.81	25.38	25.91	26.41	26.88	1.67	1.61
140	16.37	16.43	16.50	16.62	16.93	17.50	18.52	19.43	20.24	20.97	21.65	22.27	22.85	23.40	23.91	24.39	1.67	1.60
150	14.03	14.10	14.17	14.30	14.62	15.21	16.26	17.18	18.01	18.75	19.44	20.07	20.67	21.22	21.75	22.24	1.66	1.59
160	11.95	12.03	12.10	12.24	12.58	13.20	14.29	15.24	16.08	16.84	17.53	18.18	18.78	19.54	19.88	20.38	1.65	1.58
170	10.09	10.17	10.25	10.41	10.77	11.44	12.58	13.55	14.40	15.17	15.88	16.53	17.14	17.71	18.25	18.76	1.64	1.58
180		8.49	5.58	8.76	9.16	9.88	11.07	12.07	12.94	13.73	14.44	15.10	15.71	16.29	16.83	17.35	1.64	1.57
190			7.04	7.24	7.70	8.49	9.75	10.78	11.67	12.46	13.18	13.84	14.46	15.03	15.52	16.10	1.63	1.56
200				5.82	6.37	7.24	8.58	9.64	10.54	11.34	12.06	12.73	13.35	13.93	14.48	15.00	1.63	1.56
210				4.40	5.11	6.12	7.54	8.63	9.55	10.35	11.08	11.74	12.36	12.94	13.49	14.01	1.63	1.55
220					3.88	5.10	6.62	7.74	8.66	9.47	10.20	10.87	11.48	12.06	12.60	13.12	1.63	1.55
240	0.02	0.05	0.08	0.17	0.82	3.31	5.06	6.23	7.17	7.98	8.71	9.37	9.98	10.55	11.08	11.59	1.62	1.54
250	0.02	0.05	0.08	0.15	0.55	2.55	4.42	5.60	6.54	7.35	8.07	8.72	9.33	9.89	10.42	10.93	1.62	1.53
260	0.02	0.04	0.07	0.14	0.44	1.93	3.85	5.04	5.98	6.78	7.49	8.14	8.74	9.30	9.82	10.32	1.61	1.53
270	0.02	0.04	0.07	0.13	0.38	1.48	3.35	4.54	5.47	6.27	6.97	7.61	8.20	8.75	9.27	9.76	1.61	1.52
280	0.02	0.04	0.06	0.12	0.34	1.18	2.92	4.09	5.02	5.80	6.50	7.13	7.71	8.25	8.77	9.25	1.60	1.52
290	0.02	0.04	0.06	0.11	0.30	0.98	2.56	3.70	4.61	5.38	6.06	6.69	7.26	7.80	8.30	8.78	1.60	1.51
300	0.02	0.04	0.06	0.11	0.28	0.84	2.25	3.36	4.24	5.00	5.67	6.28	6.85	7.37	7.87	8.34	1.59	1.50
310	0.02	0.04	0.06	0.10	0.25	0.74	2.00	3.05	3.91	4.65	5.31	5.91	6.46	9.98	7.47	7.93	1.58	1.49
320	0.02	0.03	0.05	0.10	0.24	0.66	1.79	2.78	3.62	4.34	4.98	5.57	6.11	6.62	7.10	7.50	1.58	1.49
330	0.02	0.03	0.05	0.09	0.22	0.60	1.61	2.55	3.35	4.05	4.68	5.26	5.79	6.29	6.76	7.21	1.57	1.48
340	0.02	0.03	0.05	0.09	0.21	0.55	1.46	2.34	3.11	3.79	4.41	4.97	5.49	5.98	6.44	6.88	1.55	1.47
350	0.01	0.03	0.05	0.08	0.20	0.51	1.33	2.16	2.90	3.56	4.45	4.70	5.21	5.69	6.14	6.57	1.54	1.45
360	0.01	0.03	0.05	0.08	0.19	0.47	1.23	2.00	2.71	3.34	3.92	4.45	4.95	5.42	5.83	6.29	1.53	1.44
370	0.01	0.03	0.04	0.08	0.18	0.44	1.13	1.86	2.54	3.15	3.71	4.23	4.71	5.17	5.61	6.02	1.52	1.43
380	0.01	0.03	0.04	0.08	0.17	0.41	1.05	1.74	2.38	2.97	3.51	4.02	4.49	4.94	5.36	5.77	1.50	1.42
390	0.01	0.03	0.04	0.07	0.16	0.39	0.99	1.63	2.24	2.81	3.33	3.82	4.29	4.72	5.14	5.53	1.49	4.48
400	0.01	0.03	0.04	0.07	0.16	0.35	0.87	1.44	2.00	2.52	3.01	3.48	3.91	4.33	4.75	5.11	1.45	1.57
420	0.01	0.02	0.04	0.07	0.14	0.34	0.82	1.36	1.89	2.39	2.87	3.32	2.75	4.15	4.54	4.91	1.44	1.36

Table VIII. Configurational Internal Energy (−kJ mol^{-1}) of Tetrafluoromethane at Various Pressures (P, bar) and Temperatures (T, K)

	configurational internal energy															
T	P = 5	P = 10	P = 15	P = 25	P = 50	P = 100	P = 200	P = 300	P = 400	P = 500	P = 600	P = 700	P = 800	P = 900	P = 1000	P = 1100
95	13.251	13.256	13.261	13.272	13.297	13.346	13.437									
100	12.971	12.977	12.983	12.994	13.023	13.077	13.180	13.273	13.359							
110	12.447	12.454	12.461	12.475	12.510	12.576	12.699	12.810	12.911	13.004	13.089	13.168	13.241	13.309	13.372	13.430
120	11.960	11.968	11.977	11.994	12.035	12.114	12.257	12.385	12.501	12.606	12.702	12.790	12.872	12.947	13.017	13.081
130	11.492	11.503	11.513	11.533	11.581	11.673	11.838	11.984	12.114	12.232	12.338	12.436	12.525	12.608	12.684	12.754
140	11.027	11.040	11.052	11.075	11.132	11.239	11.429	11.594	11.739	11.869	11.986	12.093	12.190	12.279	12.361	12.457
150	10.551	10.566	12.580	10.608	10.676	10.801	11.019	11.204	11.366	11.509	11.637	11.752	11.857	11.953	12.042	12.123
160	10.054	10.072	10.090	10.124	10.205	10.352	10.602	10.810	10.989	11.146	11.285	11.410	11.523	11.626	11.720	11.806
170	9.529	9.551	9.573	9.615	9.713	9.888	10.176	10.410	10.608	10.779	10.930	11.065	11.186	11.296	11.396	11.488
180		8.995	9.023	9.076	9.199	9.410	9.744	10.007	10.225	10.412	10.575	10.719	10.849	10.966	11.072	11.170
190			8.429	8.500	8.659	8.918	9.308	9.604	9.844	10.047	10.223	10.378	10.516	10.640	10.753	10.856
200				7.867	8.085	8.414	8.873	9.206	9.470	9.691	9.880	10.045	10.192	10.324	10.443	10.552
210				7.123	7.463	7.898	8.445	8.820	9.110	9.649	9.552	9.782	9.884	10.023	10.149	10.263
220					7.769	7.392	8.051	8.473	8.792	9.049	9.267	9.454	9.619	9.766	9.898	10.018
240	0.173	0.358	0.557	1.014	3.118	5.879	6.876	7.410	7.790	8.089	8.335	8.546	8.729	8.891	9.037	9.168
250	0.166	0.341	0.527	0.942	2.419	5.377	6.620	7.218	7.631	7.951	8.212	8.434	8.626	8.796	8.948	9.085
260	0.158	0.324	0.499	0.878	2.092	4.815	6.337	7.002	7.448	7.789	8.066	8.299	8.501	8.678	8.836	8.979
270	0.151	0.308	0.472	0.822	1.872	4.268	6.036	6.770	7.250	7.612	7.903	8.148	8.358	8.543	8.708	8.856
280	0.143	0.292	0.446	0.771	1.704	3.798	5.726	6.527	7.040	7.423	7.729	7.985	8.204	8.396	8.567	8.720
290	0.137	0.277	0.422	0.725	1.568	3.416	5.417	6.279	6.825	7.227	7.547	7.814	8.042	8.241	8.418	8.576
300	0.130	0.263	0.400	0.683	1.453	3.104	5.115	6.031	6.606	7.027	7.361	7.638	7.874	8.080	8.262	8.426
310	0.124	0.250	0.379	0.645	1.353	2.847	4.826	5.784	6.386	6.825	7.172	7.458	7.702	7.975	8.105	8.271
320	0.118	0.237	0.359	0.609	1.266	2.629	4.553	5.543	6.168	6.623	6.981	7.277	7.529	7.747	7.941	8.113
330	0.112	0.226	0.341	0.576	1.188	2.441	4.297	5.308	5.953	6.422	6.792	7.092	7.354	7.579	7.777	7.954
340	0.106	0.215	0.324	0.546	1.119	2.278	4.058	5.081	5.742	6.224	6.603	6.915	7.180	7.410	7.613	7.794
350	0.101	0.204	0.308	0.518	1.055	2.134	3.838	4.863	5.536	6.029	6.417	6.736	7.007	7.242	7.450	7.635
360	0.097	0.194	0.293	0.492	0.998	2.006	3.634	4.655	5.337	5.829	6.234	6.560	6.836	7.076	7.287	7.476
370	0.092	0.185	0.279	0.467	0.945	1.890	3.445	4.457	5.144	5.653	6.055	6.386	6.667	6.911	7.126	7.318
380	0.088	0.177	0.266	0.445	0.896	1.786	3.270	4.269	4.958	5.472	5.879	6.215	6.500	6.748	6.966	7.161
390	0.084	0.168	0.253	0.424	0.851	1.691	3.109	4.090	4.779	5.296	5.708	6.048	6.337	6.588	6.809	7.007
400	0.080	0.161	0.242	0.404	0.810	1.604	2.959	3.921	4.607	5.126	5.541	5.884	6.176	6.430	6.654	6.855
410	0.077	0.154	0.231	0.385	0.771	1.524	2.819	3.760	4.442	4.962	5.379	5.724	6.019	6.276	6.502	6.705
420	0.073	0.147	0.220	0.368	0.735	1.450	2.690	3.608	4.284	4.803	5.221	5.569	5.866	6.124	5.353	6.558

Table IX. Relative Entropy (−J mol^{-1} K^{-1}) of Tetrafluoromethane at Various Pressures (P, bar) and Temperatures (T, K)

	relative entropy														
T	P = 5	P = 10	P = 15	P = 25	P = 50	P = 100	P = 200	P = 300	P = 400	P = 500	P = 600	P = 700	P = 800	P = 900	P = 1000	P = 1100
95	57.43	57.48	57.53	57.63	57.89	58.38	59.33									
100	54.65	54.70	54.76	54.87	55.14	55.67	56.68	57.64	58.55							
110	49.86	49.92	49.98	50.10	50.40	50.98	52.08	53.11	54.08	55.00	55.88	56.72	57.52	58.28	59.02	59.73
120	45.84	45.91	45.98	46.11	46.43	47.05	48.22	49.31	50.33	51.28	52.19	53.04	53.86	54.65	55.39	56.11
130	42.34	42.41	42.48	42.62	42.97	43.64	44.88	46.02	47.07	48.05	48.98	49.86	50.69	51.48	52.24	52.96
140	39.15	39.23	39.30	39.46	39.83	40.55	41.86	43.05	44.14	45.16	46.10	46.99	47.83	48.65	49.40	50.13
150	36.14	36.22	36.31	36.48	36.89	37.66	39.06	40.31	41.13	42.47	43.44	44.34	45.20	46.00	46.77	47.50
160	33.23	33.33	33.42	33.61	34.07	34.91	36.41	37.71	38.88	39.95	40.94	41.85	42.72	43.55	44.30	45.04
170	30.38	30.49	30.60	30.82	31.33	32.26	33.87	35.25	36.46	37.56	38.57	39.50	40.38	41.20	41.98	42.72
180		27.68	27.82	28.07	28.66	29.71	31.45	32.91	34.17	35.30	36.33	37.28	38.17	39.00	39.78	40.53
190			25.02	25.34	26.04	27.25	29.16	30.70	32.02	33.18	34.24	35.21	36.10	36.94	37.73	38.48
200				22.56	23.46	24.88	26.99	28.63	30.01	31.21	32.29	33.28	34.19	35.04	35.84	36.59
210				19.59	20.87	22.62	24.98	26.73	28.17	29.41	30.52	31.52	32.45	33.31	34.11	34.87
220					18.24	20.55	23.25	25.10	26.61	27.89	29.02	30.05	30.98	31.85	32.66	33.43
240	0.40	0.82	1.27	2.29	7.07	14.78	18.37	20.52	22.17	23.53	24.72	25.78	26.75	27.63	28.46	29.23
250	0.38	0.78	1.20	2.14	5.49	13.23	17.43	19.73	21.45	22.86	24.07	25.15	26.13	27.02	27.86	28.03
260	0.36	0.74	1.13	2.00	4.75	11.59	16.43	18.88	20.67	22.11	23.35	24.45	25.44	26.45	27.18	27.97
270	0.34	0.70	1.07	1.86	4.24	10.08	15.41	18.00	19.85	21.34	22.60	23.71	24.71	25.63	26.47	27.26
280	0.32	0.66	1.01	1.74	3.84	8.85	14.39	17.11	19.03	20.55	21.83	22.96	23.97	24.89	25.74	26.54
290	0.31	0.62	0.95	1.62	3.52	7.87	13.41	16.24	18.21	19.76	21.06	22.20	23.22	24.15	25.01	25.81
300	0.29	0.59	0.89	1.52	3.24	7.08	12.49	15.39	17.40	18.98	20.30	21.46	22.48	23.42	24.28	25.08
310	0.27	0.55	0.84	1.42	3.00	6.43	11.63	14.58	16.62	18.22	19.56	20.72	21.76	22.70	23.56	24.36
320	0.26	0.52	0.79	1.34	2.79	5.89	10.83	13.80	15.87	17.48	18.83	20.00	21.05	21.99	22.85	23.66
330	0.24	0.49	0.74	1.26	2.60	5.43	10.11	13.06	15.14	16.77	18.13	19.31	20.35	21.30	22.17	22.97
340	0.23	0.47	0.70	1.18	2.43	5.04	9.45	12.37	14.46	16.09	17.45	18.63	19.68	20.63	21.50	22.31
350	0.22	0.44	0.66	1.12	2.28	4.69	8.85	11.72	13.80	15.44	16.80	17.99	19.03	19.98	20.85	21.66
360	0.21	0.42	0.63	1.05	2.14	4.38	8.31	11.12	13.18	14.81	16.18	17.36	18.41	19.36	20.23	21.03
370	0.20	0.39	0.59	1.00	2.02	4.10	7.82	10.55	12.59	14.22	15.58	16.76	17.81	18.76	19.62	20.13
380	0.19	0.37	0.56	0.94	1.91	3.86	7.37	10.03	12.04	13.65	15.01	16.19	17.23	18.18	19.04	19.84
390	0.18	0.36	0.53	0.89	1.80	3.63	6.96	9.54	11.52	13.12	14.46	15.63	16.08	17.62	18.48	19.28
400	0.17	0.34	0.51	0.85	1.71	3.43	6.59	9.08	11.03	12.61	13.94	15.11	16.14	17.08	17.94	18.74
410	0.16	0.32	0.48	0.81	1.62	3.25	6.24	8.65	10.56	12.12	13.45	14.60	15.63	16.57	17.42	18.21
420	0.15	0.31	0.46	0.77	1.54	3.08	5.93	8.26	10.13	11.67	12.98	14.12	15.14	16.07	16.92	17.71

Table X. Thermodynamic Properties of Trifluoromethane along the Saturation Curve

T/K	P/bar	ρ_l/(mol dm^{-3})	ρ_v/(mol dm^{-3})	ΔH_v/(kJ mol^{-1})	$-E_\sigma$/(kJ mol^{-1})	$-S_\sigma$/(J mol^{-1} K^{-1})
130	0.0041	22.866	3.7×10^{-4}	19.778	18.699	60.535
140	0.0147	22.639	1.2×10^{-3}	19.282	18.121	56.338
150	0.0440	22.352	3.5×10^{-3}	18.812	17.575	52.671
160	0.1121	22.010	8.5×10^{-3}	18.361	17.052	49.424
170	0.2519	21.618	1.8×10^{-2}	17.913	16.542	46.484
180	0.5106	21.181	3.5×10^{-2}	17.451	16.035	43.757
190	0.9511	20.703	6.2×10^{-2}	16.960	15.521	41.166
200	1.6521	20.187	0.1043	16.423	14.992	38.661
210	2.7064	19.632	0.1665	15.825	14.442	36.208
220	4.2199	19.037	0.2551	15.153	13.868	33.791
230	6.3092	18.397	0.3786	14.391	13.267	31.403
240	9.1005	17.704	0.5479	13.525	12.640	29.044
250	12.7278	16.947	0.7787	12.535	11.983	26.715
260	17.3336	16.105	1.0946	11.390	11.294	24.418
270	23.0697	15.139	1.5351	10.044	10.563	22.146
280	30.1026	13.971	2.1768	8.407	9.772	19.883
285	34.1642	13.254	2.6216	7.424	9.338	18.743
290	38.6269	12.367	3.2048	6.268	8.859	17.584

Table XI. Mechanical Coefficients of Liquid Trifluoromethane under Saturation Conditions

T/K	$\beta \times 10^4$/bar^{-1}	$\alpha \times 10^3$/K^{-1}	γ/(bar K^{-1})	γ_σ/(bar K^{-1})	$\alpha_\sigma \times 10^3$/K^{-1}
130	0.62	0.86	13.88	0.00	0.86
140	0.73	1.14	15.50	0.00	1.14
150	0.85	1.41	16.54	0.00	1.41
160	0.99	1.67	16.90	0.01	1.67
170	1.15	1.92	16.66	0.02	1.92
180	1.36	2.17	15.97	0.03	2.16
190	1.61	2.41	14.98	0.06	2.40
200	1.94	2.67	13.79	0.09	2.65
210	2.36	2.86	12.50	0.13	2.93
220	2.95	3.29	11.18	0.18	3.24
230	3.76	3.70	9.86	0.24	3.61
240	4.94	4.24	8.57	0.32	4.08
250	6.77	1.97	7.33	0.41	4.69
260	9.86	6.07	6.16	0.51	5.56
270	15.74	7.92	5.03	0.64	6.92
280	29.74	11.75	3.95	0.77	9.45
285	46.23	15.78	3.41	0.85	11.84
290	85.75	24.48	2.86	0.93	16.47

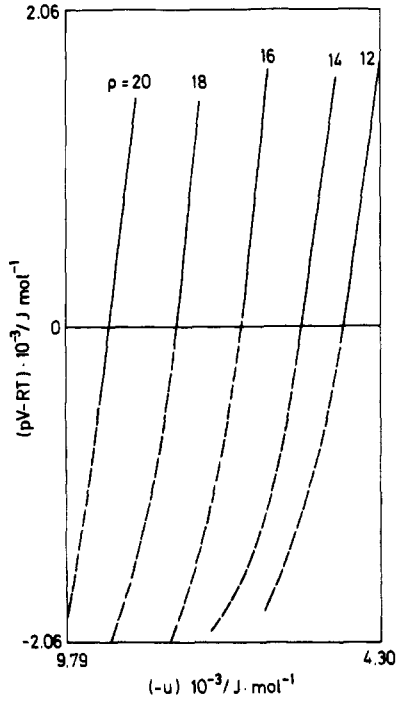

Figure 7. Test of eq 6 for CO_2. The numbers indicate the density in mol dm^{-3}. The dashed lines indicate the region for which eq 6 does not hold.

Malesinski (*26*) has shown that from eq 3 and the virial theorem it is possible to derive

$$pV - RT = \frac{n}{3}\langle U\rangle - \left(\frac{n}{3} - \frac{m}{3}\right)\langle U_a\rangle \qquad (6)$$

with the configurational energy $\langle U\rangle$ given by

$$\langle U\rangle = \frac{N^2}{2V}\int U_{eff}(r,T,V)\, g(r,T,V)\, d\vec{r} \qquad (7)$$

Figures 7–9 show $pV - RT$ vs $\langle U\rangle$ for three different substances: CO_2, C_2H_4, and CHF_3. The data for CHF_3 are those reported in this work, while those for CO_2 and C_2H_4 were taken from refs 27 and 28, respectively. It can be observed that the linear behavior predicted by eq 6 along an isochore is limited to the high-density high-temperature region for which many perturbation theories of fluids have been developed (*29*). Even for that region, the apparent validity of eq 6 (which implies that $\langle U_a\rangle$ is constant along each isochore) is in contradiction with

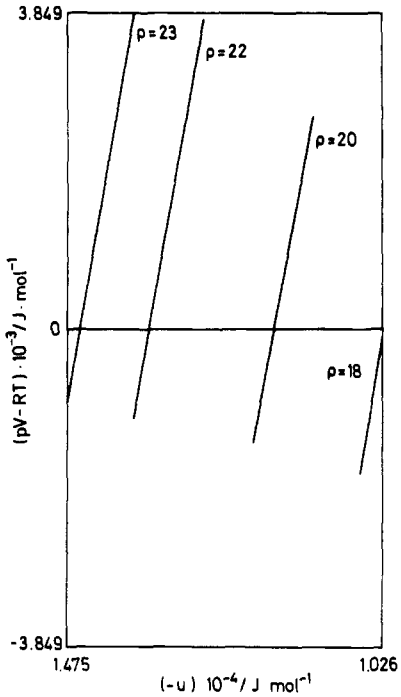

Figure 8. Test of eq 6 for C_2H_4. Additional details are as given in Figure 7.

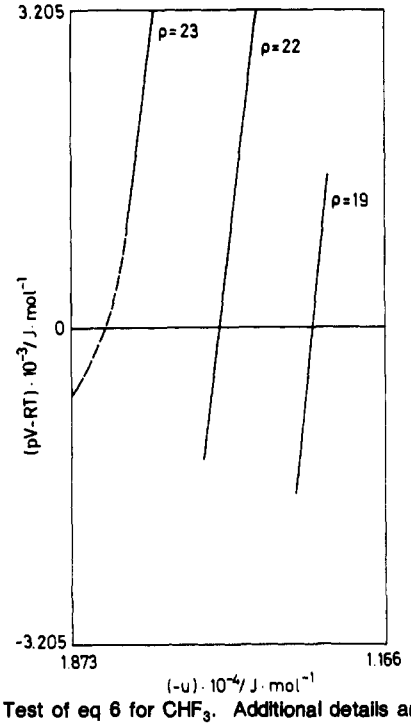

Figure 9. Test of eq 6 for CHF_3. Additional details are as given in Figure 7.

the failure of eq 4 (see Figure 6).

Fixing $m = 6$, the slopes of the lines shown in Figures 7–9 lead to the following values of $\langle n\rangle$: 14, 9, 10, and 21 for C_2H_4, CO_2, CHF_3, and CF_4, respectively. It should be pointed out that while n is almost density-independent for C_2H_4, with only a 1% scattering around $\langle n\rangle = 14$, for CO_2 and CHF_3 n changes up to 20% in the density ranges of Figures 7 and 9 and the variation of n rises up to a maximum of 30% for CF_4. This density dependence of n again is an indication of the weakness of the spherical effective potential model, eq 3, even for relatively simple molecular fluids like the ones considered in this work. Even though the value $\langle n\rangle = 21$ obtained for CF_4 agrees quite well with that used in ref 3, and with the one obtained by Compostizo et al. (*24*), the small value obtained for CHF_3 is

Table XII. Density (mol dm^{-3}) of Trifluoromethane at Round Values of Pressure (P, bar) and Temperature (T, K)

	density														
T	P = 5	P = 10	P = 15	P = 25	P = 50	P = 100	P = 200	P = 300	P = 400	P = 500	P = 600	P = 700	P = 800	P = 900	P = 1000
130	22.873	22.880	22.887	22.902	22.937	23.006	23.141	23.271	23.398	23.521	23.640	23.756	23.869	23.979	24.086
140	22.647	22.655	22.664	22.680	22.721	22.801	22.956	23.103	23.245	23.382	23.523	23.640	23.763	23.882	23.997
150	22.362	22.371	22.380	22.399	22.446	22.537	22.711	22.876	23.033	23.182	23.325	23.462	23.594	23.721	23.844
160	22.020	22.031	22.042	22.063	22.116	22.219	22.414	22.597	22.769	22.932	23.086	23.234	23.375	23.510	23.640
170	21.629	21.642	21.654	21.679	21.739	21.855	22.073	22.275	22.464	22.641	22.808	22.967	23.117	23.262	23.400
180	21.194	21.208	21.222	21.250	21.319	21.451	21.696	21.920	22.126	22.319	22.500	22.670	22.932	22.985	23.132
190	20.717	20.733	20.750	20.782	20.861	21.012	21.287	21.536	21.763	21.973	22.169	11.352	22.525	22.689	22.844
200	20.200	20.219	20.238	20.276	20.368	20.541	20.853	21.130	21.380	21.609	21.821	22.018	22.203	22.378	22.543
210	19.643	19.666	19.688	19.733	19.841	20.042	20.397	20.706	20.982	21.232	21.461	21.673	21.871	22.057	22.232
220	19.041	19.069	19.096	19.150	19.278	19.513	19.920	20.266	20.571	20.844	21.092	21.320	21.532	21.730	21.916
230		18.422	18.456	18.522	18.677	18.956	19.425	19.814	20.150	20.448	20.717	20.962	21.189	21.399	21.597
240		17.712	17.755	17.838	18.031	18.367	18.911	19.350	19.722	20.047	20.338	20.601	20.843	21.067	21.276
250			16.973	17.083	17.330	17.743	18.380	18.876	19.287	19.643	19.957	20.240	20.298	20.736	20.957
260				16.222	16.555	17.077	17.831	18.393	18.848	19.236	19.575	19.878	20.153	20.405	20.639
270				15.185	15.673	16.359	17.263	17.901	18.405	18.828	19.193	19.518	19.810	20.077	20.323
280					14.615	15.573	16.673	17.401	17.959	18.419	18.813	19.160	19.470	19.752	20.012
290					13.184	14.695	16.061	16.892	17.511	18.011	18.435	18.804	19.134	19.432	19.704
310	0.201	0.417	0.651	1.193	3.588	12.474	14.759	15.852	16.609	17.198	17.686	18.105	18.473	18.803	19.103
320	0.194	0.400	0.621	1.120	2.980	10.960	14.064	15.321	16.156	16.795	17.316	17.761	18.149	18.496	18.103
330	0.187	0.385	0.595	1.059	2.630	9.142	13.338	14.782	15.703	16.393	16.950	17.421	17.830	18.193	18.521
340	0.181	0.371	0.571	1.006	2.388	7.436	12.584	14.238	15.251	15.994	16.688	17.086	17.516	17.896	18.238

Table XIII. Isothermal Compressibility (10^{-4}/bar) for Trifluoromethane at Various Pressures (P, bar) and Temperatures (T, K)

	isothermal compressibility														
T	P = 5	P = 10	P = 15	P = 25	P = 50	P = 100	P = 200	P = 300	P = 400	P = 500	P = 600	P = 700	P = 800	P = 900	P = 1000
130	0.62	0.62	0.62	0.62	0.61	0.60	0.57	0.55	0.53	0.51	0.50	0.48	0.47	0.45	0.44
140	0.73	0.73	0.73	0.72	0.71	0.69	0.66	0.63	0.60	0.57	0.55	0.53	0.51	0.49	0.47
150	0.85	0.85	0.84	0.84	0.82	0.80	0.75	0.70	0.66	0.63	0.60	0.57	0.55	0.53	0.51
160	0.99	0.98	0.98	0.97	0.95	0.91	0.84	0.78	0.73	0.69	0.65	0.62	0.59	0.56	0.54
170	1.15	1.14	1.14	1.12	1.09	1.04	0.95	0.88	0.81	0.76	0.71	0.67	0.64	0.61	0.58
180	1.35	1.34	1.33	1.31	1.27	1.20	1.08	0.98	0.90	0.84	0.78	0.73	0.69	0.65	0.62
190	1.60	1.59	1.57	1.55	1.49	1.39	1.23	1.10	1.00	0.92	0.85	0.80	0.75	0.70	0.66
200	1.92	1.90	1.89	1.85	1.77	1.62	1.40	1.24	1.12	1.02	0.93	0.87	0.81	0.76	0.71
210	2.35	2.32	2.29	2.24	2.12	1.92	1.62	1.41	1.25	1.12	1.03	0.94	0.88	0.82	0.77
220	2.94	2.89	2.85	2.77	2.58	2.28	1.87	1.60	1.40	1.25	1.13	1.03	0.95	0.88	0.82
230		3.70	3.63	3.49	3.20	2.76	2.18	1.82	1.56	1.38	1.24	1.12	1.03	0.95	0.89
240		4.92	4.79	4.55	4.07	3.37	2.55	2.07	1.76	1.53	1.36	1.22	1.12	1.03	0.95
250			6.66	6.21	5.33	4.20	3.01	2.37	1.97	1.69	1.49	1.53	1.21	1.10	1.02
260				9.09	7.30	5.34	3.57	2.72	2.21	1.88	1.63	1.45	1.30	1.19	1.09
270				15.20	10.73	6.98	4.26	3.12	2.49	2.08	1.79	1.57	1.41	1.27	1.17
280					17.84	9.40	5.13	3.60	2.79	2.30	1.96	1.71	1.52	1.37	1.24
290					39.73	13.48	6.24	4.15	3.14	2.54	2.14	1.85	1.63	1.46	1.33
310	2071.7	1077.8	751.8	505.4	475.1	34.80	9.44	5.55	3.96	3.09	2.54	2.16	1.88	1.67	1.50
320	2062.5	1067.0	738.9	485.5	356.1	65.35	11.76	6.43	4.44	3.40	2.76	2.33	2.02	1.78	1.59
330	2054.6	1057.8	728.2	470.4	307.3	117.2	14.73	7.44	4.98	3.74	3.00	2.51	2.15	1.89	1.69
340	2047.6	1050.0	719.3	458.7	279.9	152.1	18.45	8.61	5.57	4.11	3.25	2.69	2.30	2.01	1.78

Table XIV. Thermal Expansion Coefficient (10^{-3} K^{-1}) for Trifluoromethane at Various Pressures (P, bar) and Temperatures (T, K)

	thermal expansion coefficient														
T	P = 5	P = 10	P = 15	P = 25	P = 50	P = 100	P = 200	P = 300	P = 400	P = 500	P = 600	P = 700	P = 800	P = 900	P = 1000
130	0.86	0.85	0.85	0.84	0.81	0.76	0.67	0.59	0.51	0.45	0.39	0.34	0.29	0.25	0.22
140	1.13	1.13	1.12	1.11	1.08	1.03	0.94	0.86	0.79	0.73	0.68	0.63	0.59	0.55	0.52
150	1.41	1.40	1.39	1.38	1.35	1.30	1.20	1.11	1.04	0.98	0.92	0.87	0.83	0.79	0.76
160	1.67	1.66	1.65	1.64	1.60	1.54	1.43	1.34	1.26	1.19	1.13	1.07	1.03	0.98	0.95
170	1.91	1.91	1.90	1.88	1.84	1.76	1.63	1.53	1.44	1.36	1.29	1.23	1.18	1.13	1.09
180	2.16	2.14	2.13	2.11	2.06	1.97	1.81	1.69	1.59	1.50	1.43	1.36	1.30	1.25	1.21
190	2.40	2.38	2.37	2.34	2.28	2.17	1.98	1.84	1.72	1.62	1.53	1.46	1.40	1.34	1.29
200	2.66	2.64	2.62	2.59	2.50	2.36	2.14	1.97	1.83	1.72	1.63	1.55	1.48	1.41	1.36
210	2.95	2.92	2.90	2.85	2.75	2.56	2.29	2.09	1.93	1.81	1.70	1.61	1.54	1.47	1.41
220	3.29	3.25	3.22	3.16	3.01	2.78	2.44	2.20	2.02	1.88	1.77	1.67	1.59	1.51	1.45
230		3.67	3.62	3.53	3.33	3.02	2.60	2.31	2.11	1.95	1.82	1.72	1.63	1.55	1.48
240		4.22	4.15	4.01	3.72	3.30	2.76	2.42	2.19	2.01	1.87	1.75	1.66	1.58	1.51
250			4.91	4.69	4.24	3.63	2.94	2.54	2.27	2.07	1.91	1.79	1.69	1.60	1.52
260				5.74	4.96	4.04	3.13	2.65	2.34	2.12	1.95	1.82	1.71	1.61	1.53
270				7.73	6.08	4.58	3.35	2.77	2.42	2.17	1.99	1.84	1.72	1.63	1.54
280					8.14	5.31	3.60	2.90	2.49	2.22	2.02	1.86	1.74	1.63	1.55
290					13.55	6.36	3.89	3.03	2.57	2.26	2.05	1.88	1.75	1.64	1.55
310	3.68	4.22	4.87	6.69	24.43	10.78	4.61	3.33	2.72	2.35	2.10	1.91	1.77	1.65	1.55
320	3.52	3.98	4.52	5.94	14.63	15.44	5.05	3.49	2.80	2.40	2.12	1.93	1.77	1.65	1.55
330	3.38	3.77	4.23	5.36	10.80	20.39	5.55	3.66	2.88	2.44	2.15	1.94	1.78	1.65	1.54
340	3.25	3.59	3.97	4.90	8.69	19.91	6.10	3.84	2.97	2.48	2.17	1.95	1.78	1.65	1.54

Table XV. Thermal Pressure Coefficient (bar/K) for Trifluoromethane at Various Pressures (P, bar) and Temperatures (T, K)

	thermal pressure coefficient														
T	P = 5	P = 10	P = 15	P = 25	P = 50	P = 100	P = 200	P = 300	P = 400	P = 500	P = 600	P = 700	P = 800	P = 900	P = 1000
130	13.82	13.76	13.70	13.58	13.29	12.73	11.64	10.62	9.66	8.75	7.89	7.08	6.31	5.59	4.91
140	15.47	15.43	15.40	15.34	15.18	14.86	14.27	13.73	13.23	12.76	12.33	11.93	11.56	11.21	10.89
150	16.53	16.52	16.50	16.48	16.41	16.29	16.07	15.87	15.69	15.54	15.40	15.28	15.17	15.07	14.99
160	16.90	16.90	16.91	16.91	16.92	16.94	16.99	17.04	17.10	17.17	17.24	17.31	17.38	17.46	17.54
170	16.68	16.69	16.70	16.73	16.80	16.93	17.19	17.44	17.67	17.89	18.11	18.32	18.53	18.73	18.92
180	16.00	16.02	16.04	16.09	16.21	16.43	16.86	17.25	17.62	17.96	18.29	18.61	18.91	19.19	19.47
190	15.01	15.04	15.07	15.14	15.29	15.60	16.16	16.67	17.14	17.58	18.00	18.39	18.76	19.11	19.45
200	13.82	13.86	13.90	13.98	14.18	14.55	15.23	15.84	16.39	15.91	17.39	17.83	18.26	18.66	19.04
210	15.23	12.58	12.62	12.72	12.95	13.39	14.17	14.86	15.48	16.05	16.58	17.08	17.54	17.98	18.40
220	11.19	11.24	11.30	11.41	11.68	12.17	13.05	13.81	14.49	15.11	15.68	16.21	16.70	17.17	17.61
230		9.91	9.97	10.10	10.40	10.96	11.92	12.75	13.47	14.13	14.73	15.28	15.80	16.28	16.74
240		8.58	8.66	8.81	9.16	9.78	10.82	11.70	12.47	13.15	13.77	14.35	14.88	15.37	15.84
250			7.38	7.55	7.95	8.64	9.77	10.70	11.50	12.20	12.84	13.43	13.97	14.47	14.95
260				6.32	6.79	7.57	8.79	9.75	10.58	11.30	11.95	12.54	13.09	13.60	14.07
270				5.09	5.67	6.56	7.86	8.87	9.71	10.45	11.10	11.70	12.25	12.76	13.23
280					4.56	5.61	7.01	8.06	8.91	9.65	10.31	10.91	11.46	11.96	12.44
290					3.41	4.72	6.23	7.31	8.17	8.92	9.58	10.17	10.72	11.22	11.69
310	0.02	0.04	0.06	0.13	0.51	3.10	4.88	6.00	6.88	7.62	8.27	8.85	9.38	9.87	10.33
320	0.02	0.04	0.06	0.12	0.41	2.36	4.29	5.43	6.31	7.05	7.69	8.27	8.79	9.27	9.72
330	0.02	0.04	0.06	0.11	0.35	1.74	3.77	4.92	5.80	6.53	7.16	7.73	8.24	8.71	9.15
340	0.02	0.03	0.06	0.11	0.31	1.31	3.31	4.46	5.33	6.05	6.67	7.23	7.73	8.20	8.63

Table XVI. Configurational Internal Energy (−kJ mol^{-1}) of Trifluoromethane at Various Pressures (P, bar) and Temperatures (T, K)

	configurational internal energy														
T	P = 5	P = 10	P = 15	P = 25	P = 50	P = 100	P = 200	P = 300	P = 400	P = 500	P = 600	P = 700	P = 800	P = 900	P = 1000
130	18.701	18.703	18.705	18.710	18.721	18.743	18.779	18.808	18.831	18.847	18.859	18.865	18.868	18.866	18.361
140	18.124	18.128	18.131	18.138	18.155	18.186	18.242	18.289	18.330	18.364	18.393	18.417	18.437	18.452	18.464
150	17.579	17.583	17.588	17.597	17.620	17.663	17.740	17.808	17.868	17.921	17.968	18.009	18.046	18.078	18.106
160	17.057	17.063	17.069	17.081	17.110	17.165	17.265	17.355	17.434	17.506	17.570	17.628	17.681	17.728	17.772
170	16.549	16.556	16.564	16.578	16.614	16.683	16.807	16.918	17.017	17.107	17.188	17.262	17.330	17.392	17.449
180	16.043	16.052	16.061	16.079	16.123	16.205	16.355	16.488	16.607	16.714	16.812	16.901	16.983	17.058	17.128
190	15.530	15.541	15.551	15.573	15.625	15.723	15.900	16.056	16.194	16.319	16.433	16.537	16.632	16.720	16.802
200	15.000	15.013	15.026	15.052	15.113	15.229	15.435	15.615	15.744	15.917	16.046	16.164	16.272	16.372	16.464
210	14.449	14.464	14.480	14.510	14.583	14.719	14.957	15.162	15.342	15.503	15.648	15.779	15.900	16.011	16.133
220	13.870	13.889	13.907	13.944	14.031	14.190	14.465	14.697	14.899	15.077	15.237	15.383	15.515	15.637	15.749
230		13.284	13.306	13.350	13.455	13.642	13.958	14.220	14.445	14.642	14.817	14.976	15.120	12.252	15.373
240		12.644	12.672	12.727	12.854	13.077	13.441	13.735	13.985	14.199	14.390	14.562	14.717	14.859	14.989
250			11.999	12.068	12.227	12.496	12.916	13.246	13.520	13.756	13.963	14.147	14.313	13.465	14.604
260				11.365	11.571	11.902	12.391	12.761	13.062	13.318	13.541	13.738	13.916	14.076	14.223
270				10.589	10.879	11.300	11.875	12.290	12.620	12.897	13.136	13.346	13.534	13.704	13.858
280					10.134	10.700	11.384	11.850	12.212	12.511	12.766	12.990	13.188	13.366	13.528
290					9.290	10.143	10.971	11.496	11.892	12.214	12.486	12.722	12.930	13.117	13.286
310	0.254	0.522	0.806	1.435	3.791	9.151	10.471	11.140	11.612	11.983	12.290	12.552	12.781	12.983	13.165
320	0.242	0.494	0.760	1.337	3.233	8.444	10.205	10.964	11.480	11.877	12.201	12.476	12.715	12.925	13.114
330	0.230	0.469	0.718	1.251	2.879	7.506	9.888	10.750	11.312	11.736	12.079	12.367	12.615	12.833	13.027
340	0.219	0.446	0.680	1.175	2.617	6.515	9.520	10.500	11.112	11.564	11.925	12.226	12.484	12.710	12.910

Table XVII. Relative Entropy (−J mol^{-1} K^{-1}) for Trifluoromethane at Various Pressures (P, bar) and Temperatures (T, K)

	relative entropy														
T	P = 5	P = 10	P = 15	P = 25	P = 50	P = 100	P = 200	P = 300	P = 400	P = 500	P = 600	P = 700	P = 800	P = 900	P = 1000
130	60.55	60.57	60.58	60.61	60.69	60.84	61.10	61.32	61.51	61.67	61.81	61.92	62.02	62.09	62.15
140	56.36	56.38	56.40	56.45	56.55	56.76	57.13	57.57	57.77	58.05	58.30	58.53	58.75	58.94	59.13
150	52.70	52.73	52.75	52.81	52.94	53.20	53.69	54.14	54.55	54.93	55.29	55.63	55.94	56.24	56.52
160	49.46	49.49	49.52	49.59	49.75	50.07	50.66	51.21	51.71	52.19	51.64	53.06	53.46	53.84	54.20
170	46.52	46.56	46.60	46.68	46.87	47.24	47.93	48.56	49.15	49.71	50.23	50.72	51.19	51.64	52.07
180	43.80	43.80	43.89	43.98	44.19	44.61	45.40	46.11	46.78	47.40	47.99	48.54	49.07	49.57	50.05
190	41.20	41.26	41.31	41.41	41.66	42.13	43.00	43.79	44.52	45.21	45.85	46.45	47.02	47.57	48.09
200	38.70	38.76	38.81	38.93	39.20	39.73	40.69	41.55	42.35	43.08	43.77	44.42	45.03	45.62	46.17
210	36.24	36.30	36.37	36.49	36.80	37.38	38.43	39.37	40.22	41.01	41.74	42.43	43.07	43.69	44.27
220	33.80	33.88	33.95	34.09	34.44	35.08	36.23	37.24	38.15	39.98	39.75	40.47	41.15	41.79	42.40
230		31.47	31.55	31.71	32.10	32.82	43.07	35.16	36.12	37.00	37.80	38.55	39.26	39.92	40.55
240		29.06	29.16	29.35	29.80	30.61	31.97	33.13	34.15	35.07	35.91	36.69	37.41	38.10	38.74
250			26.77	27.00	27.52	28.44	29.95	31.19	32.26	33.22	34.09	34.89	35.64	36.34	37.00
260				24.64	25.28	26.35	28.01	29.34	30.47	31.47	32.37	33.19	33.96	34.67	35.35
270				22.22	23.06	24.34	26.19	27.61	28.80	29.84	30.77	31.62	32.40	33.13	33.81
280					20.85	22.45	24.54	26.07	27.33	28.41	29.36	30.23	31.03	31.77	32.46
290					18.62	30.84	23.25	24.89	26.21	27.33	28.32	29.21	30.02	30.77	31.47
310	0.54	1.10	1.69	3.00	7.77	18.53	21.94	23.87	25.33	26.54	27.58	28.50	29.34	30.10	30.81
320	0.51	1.03	1.59	2.78	6.64	17.01	21.29	23.39	24.93	26.17	27.24	28.18	29.03	29.80	30.52
330	0.48	0.98	1.49	2.59	5.90	15.08	20.51	22.81	24.43	25.72	26.81	27.77	28.63	29.41	30.13
340	0.45	0.92	1.40	2.42	5.34	13.08	19.63	22.14	23.85	25.18	26.30	27.28	28.14	28.93	29.66

somewhat surprising, and it is perhaps related to the simultaneous existence of anisotropy of shape and multipolar interactions.

Registry No. CF_4, 75-73-0; CF_3H, 75-46-7.

Literature Cited

(1) Powles, J. C.; Evans, W. A.; McGrath, E.; Gubbins, K. E.; Murad, S. *Mol. Phys.* **1979**, *38*, 893.
(2) Calado, J. C. G.; Clancy, P.; Heintz, A.; Streett, W. B. *J. Chem. Eng. Data* **1982**, *27*, 376.
(3) Rubio, R. G.; Calado, J. C. G.; Clancy, P.; Streett, W. B. *J. Phys. Chem.* **1985**, *89*, 4637.
(4) Pass, R.; Schneider, G. M. *J. Chem. Thermodyn.* **1979**, *11*, 267.
(5) Wirths, M.; Schneider, G. M. *Fluid Phase Equilib.* **1985**, *21*, 257.
(6) Rubio, R. G.; Zollweg, J. A.; Streett, W. B. *Ber. Bunsen-Ges. Phys. Chem.* **1989**, *93*, 791.
(7) Stewart, R. B.; Jacobson, R. T.; Becker, J. H.; Zimmerman, M. J. A Survey of the Thermodynamic Property Data for the Halocarbon Refrigerants. Technical Report No. 81'2; Center for Applied Thermodynamics: University of Idaho: Moscow, ID, 1981.
(8) Strobridge, T. R. Technical Note No. 129A; National Bureau of Standards: Gaithersburg, MD, 1963.
(9) Lobo, L. Q.; Staveley, L. A. K. *J. Chem. Eng. Data* **1981**, *26*, 404.
(10) Terry, M. J.; Lynch, J. T.; Bunclark, M.; Mansell, K. R.; Staveley, L. A. K. *J. Chem. Thermodyn.* **1969**, *1*, 413.
(11) McCormack, K. E.; Schneider, W. G. *J. Chem. Phys.* **1951**, *19*, 849.
(12) Kratzke, H.; Niepmann, R.; Spillner, E.; Kohler, E. *Fluid Phase Equilib.* **1984**, *16*, 287.
(13) Smith, J. H.; Pace, E. L. *J. Phys. Chem.* **1969**, *73*, 4232.
(14) Bagloi, Y. P.; Butko, A. E.; Mikhailenko, S. A.; Yukaba, V. V. *Russ. J. Phys. Chem. (Engl. Transl.)* **1988**, *42*, 564.
(15) Valentine, R. H.; Brodale, G. E.; Glauque, W. F. *J. Am. Chem. Soc.* **1962**, *66*, 392.
(16) Hori, K.; Okazaki, S.; Uematsu, M.; Watanabe, K. In *Proceedings of the 8th Symposium on Thermophysical Properties*, Gaithersburg, MD, 1981; Sengers, J. V., Ed.; American Society of Mechanical Engineers: New York, 1982.
(17) Hou, Y. C.; Martin, J. J. *AIChE J.* **1959**, *5*, 125.
(18) Goodwin, R. D. The Thermophysical Properties of Methane from 90 to 500 K at Pressures to 700 Bar; Technical Note No. 653; National Bureau of Standards: Washington, D.C., 1974.
(19) Kondo, H.; Watanabe, K.; Tanishita, I. *Bull. JSME* **1974**, *17*, 776; **1974**, *17*, 783.
(20) Dymond, J. H.; Smith, E. B. *The Virial Coefficients of Pure Gases and Mixtures*; Clarendon Press: Oxford, U.K., 1980.
(21) Bohm, H. J.; Ahlrichs, R.; Scharf, P.; Schiffler, H. *J. Chem. Phys.* **1984**, *81*, 1389.
(22) Bohn, M.; Fischer, J.; Kohler, F. *Fluid Phase Equilib.* **1986**, *31*, 233.
(23) Huang, Y. H.; O'Connell, J. P. *Fluid Phase Equilib.* **1987**, *37*, 75.
(24) Compostizo, A.; Crespo Colin, A.; Vigil, M. R.; Rubio, R. G.; Díaz, Peña, M. *Chem. Phys.* **1989**, *130*, 177.
(25) Grindley, T.; Lind, J. E. *J. Chem. Phys.* **1978**, *68*, 5046.
(26) Malesinski, W. In *Proceedings of the 1st International Conference of Calorimetry and Thermodynamics*; Malesinski, W., Ed.; Polish Science Publisher: Warsaw, 1969.
(27) Angus, S.; Armstrong, B.; de Reuck, K. N. Carbon Dioxide. *International Thermodynamic Tables of the Fluid State*; Pergamon Press: Oxford, U.K., 1976.
(28) Angus, S.; Armstrong, B.; de Reuck, K. M. Ethylene. *International Thermodynamic Tables of the Fluid State*; Pergamon Press: Oxford, U.K., 1974.
(29) Gray, C. G.; Gubbins, K. E. *Theory of molecular fluids*; Clarendon Press: Oxford, U.K., 1984.
(30) Douslin, D. R.; Harrison, R. H.; Moore, R. T.; McCullough, J. P. *J. Chem. Phys.* **1961**, *35*, 1357.
(31) Lange, H. R.; Stein, F. P. *J. Chem. Eng. Data* **1970**, *15*, 56.
(32) Martin, J. J.; Bhada, R. K. *AIChE J.* **1971**, *17*, 683.
(33) Belzile, J. L.; Kallaguine, S.; Ramalho, R. S. *Can. J. Chem. Eng.* **1976**, *54*, 450.

Received for review April 20, 1990. Accepted November 14, 1990. This work was supported in part by Universidad Complutense under a grant for Grupos Precompetitivos and by CICYT under Grant CB86-0159.

Isobaric Vapor–Liquid Equilibrium Data for the Binary Systems 1,2-Dimethoxyethane + Alcohols

José Luis Cabezas and Sagrario Beltrán

Department of Chemical Engineering, University College, 09002 Burgos, Spain

José Coca*

Department of Chemical Engineering, University of Oviedo, 33071 Oviedo, Spain

Vapor–liquid equilibrium data are reported at 101.32 kPa for the binary systems formed by 1,2-dimethoxyethane with the following alcohols: methanol, ethanol, 1-propanol, and 1-butanol. An azeotrope was observed for the systems ethanol + 1,2-dimethoxyethane and 1,2-dimethoxyethane + 1-propanol. Experimental data, activity coefficients, fugacity coefficients, and correlation parameters for the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations are reported.

Introduction

Experimental data of vapor–liquid equilibrium (VLE) are useful for designing some types of separation processes. When experimental data are not available, estimations are made, based mainly on group contribution models (*1*). Hank et al. (*2*) proposed a method for predicting VLE data from excess molar enthalpies H^E at different temperatures.

In this paper we report VLE data for 1,2-dimethoxyethane (2,5-dioxahexane) + 1-alkanol (methanol through butanol) systems. Excess molar enthalpy data at 298.15 K are available for all these systems (*3*), but no VLE measurements have been published. The data reported here will be used as part of a program to determine the applicability of liquid models for the calculation of activity coefficients (*4*).

Experimental Section

Apparatus and Procedure. Vapor–liquid equilibrium measurements were carried out in an all-glass equilibrium still of the Gillespie type (*5*) as modified by Röck and Sieg (*6*). It is a commercial unit manufactured by Fritz GmbH (Normag, Hofheim, Germany), and its features have been described previously (*7*). The apparatus allows good mixing of the vapor and liquid phases and good separation of the phases once they reach equilibrium, and it prevents entrainment of liquid drops and partial condensation in the vapor phase.

The boiling point temperature T in the equilibrium still was measured with a mercury-in-glass thermometer (0.1 K divisions),

* To whom correspondence should be addressed.

0021-9568/91/1736-0184$02.50/0