Vapor pressures, liquid molar volumes, vapor non-idealities, and critical properties of some fluorinated ethers: $CF_3OCF_2OCF_3$, $CF_3OCF_2CF_2H$, c-$CF_2CF_2CF_2O$, CF_3OCF_2H, and CF_3OCH_3; and of CCl_3F and CF_2ClH

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Vapor pressures, compressibilities, expansivities, and molar volumes of the liquid phase have been measured between room temperature and the critical temperature for a series of fluorinated ethers: $CF_3OCF_2OCF_3$, $CF_3OCF_2CF_2H$, c-$CF_2CF_2CF_2O$, CF_3OCF_2H, and CF_3OCH_3. Vapor-phase non-idealities were measured for each compound, but only for samples of high vapor density. Critical temperatures and pressures and approximate melting and boiling temperatures are reported. Apparatus calibrations were checked with measurements on the well characterized materials: $CFCl_3$, (R11) and CF_2ClH (R22).

1. Introduction

The expected commercial ban on many of the lower-molar-mass chlorofluoro-carbons has prompted a vigorous search for substitute compounds to use in refrigeration, and as blowing agents and cleaning fluids.[1] Ideally, the substitute compounds will be similar enough to the freons in their physical and chemical properties to permit simple replacement in a given process, and will not require extensive redesign or replacement of machinery. Also, the new compounds should have lower ozone-depletion indices and lower "greenhouse gas" warming effects. In this paper we report measurements on the physical properties of a series of fluorinated ethers designed to meet these criteria. In order to test the experimental techniques we also measured the physical properties of $CFCl_3$ (R11) and CF_2ClH (R22), compounds which are already well characterized.

2. Experimental

Perfluorodimethoxymethane ($CF_3OCF_2OCF_3$), 2-hydryl-*F*-ethyl *F*-methyl ether ($CF_3OCF_2F_2H$), *F*-oxetane (c-$CF_2CF_2CF_2O$), pentafluorodimethyl ether

(CF$_3$OCF$_2$H), and F-methyl methyl ether (CF$_3$OCH$_3$) were prepared by Adcock et al.[2] using the aerosol fluorination technique developed by Adcock and coworkers.[3] After initial work-up of the reaction products and purification by trap-to-trap distillation, the ethers were purified by preparative-scale g.c. The collected fractions were dried over molecular sieves and transferred as the vapor to a stainless-steel vessel for storage. They were analyzed by capillary g.c. (HP-5980A) and in each case showed mole-fraction purities in excess of 0.9998.

Liquid densities were determined as a function of temperature and pressure in two ways. For (298 < T/K < 373 or T/T^c = 0.92), whichever upper bound was less, and (0.1 < p/MPa < 35) we employed a Mettlar-Paar vibrating DMA-05 densitometer connected to an HIP 62-6-10 screw-type pressure generator and followed the techniques described by Matsuo and Van Hook.[4] Calibrations against nitrogen,[5] water,[6] benzene,[7 9] and tetrachloromethane[10] were fitted by least squares to deduce parameters for the working equation of the densitometer reported in the form:

$$10^{-3} \cdot \rho/(kg \cdot m^{-3}) = \sum_{i=0}^{2} A_i \cdot (t_i/K) + A_3 \cdot (p/MPa)$$
$$+ \left\{ \sum_{i=0}^{2} B_i \cdot (t_i/K) + B_3 \cdot (p/MPa) \right\} \cdot (\tau/kHz)^2 + C_0 \cdot (\tau/kHz)^4. \quad (1)$$

The parameters of equation (1) are reported in table 1, $t = (T - 273.15 \text{ K})$, and τ is the densitometer vibrational frequency. The 373 K and 35 MPa temperature and pressure bounds were imposed by the thermostat and densitometer design, respectively. We have been unable to obtain results of useful precision using vibrating densitometry for temperatures close to T^c and therefore selected $(T^c - T) = 25 \text{ K}$ as a working upper bound for those compounds with $T^c < 398 \text{ K}$.

In the second method used to determine density and its derived properties: molar volume, expansivity, and compressibility, measurements from room temperature to the critical temperature, and at pressures from 0.1 MPa to 6 MPa, were made in the (p, V_m, T) apparatus described by Kooner and Van Hook[7] and Salvi and Van Hook.[11] Samples were forced from a thermostatted and calibrated screw injector (S.I.) into the measuring cell while pressure was monitored. The amounts of material in the S.I. and connecting lines before and after the sample had been injected into the calibrated measuring cell were calculated from p and $T_{S.I.}$ using equation (4) and table 5. Thus, all molar-volume measurements ultimately referred back to the vibrating densitometry. The initial part of the (n_{inj}, p) curve (i.e. that part before condensation) permitted vapor non-ideality to be determined from the known cell volume. Here n_{inj} is the total amount of substance injected from the S.I. into the measuring cell. The precision was determined by the relative error: $\delta n_{inj}/n_{inj}$, which is

TABLE 1. The parameters of equation (1):

$$10^{-3} \cdot \rho/(kg \cdot m^{-3}) =$$
$$\sum_{i=0}^{2} A_i \cdot (t_i/K) + A_3 \cdot (p/MPa) + \left\{ \sum_{i=0}^{2} B_i \cdot (t_i/K) + B_3 \cdot (p/MPa) \right\} \cdot (\tau/kHz)^2 + C_0 \cdot (\tau/kHz)^4$$

$A_0 = -4.572521$; $A_1 = -2.385628 \cdot 10^{-3}$; $A_2 = 2.646661 \cdot 10^{-5}$; $A_3 = 4.880443 \cdot 10^{-4}$.
$B_0 = 0.365672$; $B_1 = 0$; $B_2 = -1.732134 \cdot 10^{-6}$; $B_3 = -4.490327 \cdot 10^{-5}$; $C_0 = 1.891651 \cdot 10^{-4}$.
$10^{-6} \cdot \sigma^2/(kg^2 \cdot m^{-6}) = 3.7 \cdot 10^{-8}$ where σ denotes the variance

large when n_{inj} is small, and the vapor-density results were useful only when the sample temperature was high and n_{inj}(vapor) was reasonably large (*i.e.* for $p > 0.3$ MPa or so). Upon condensation the cell filled at the sample vapor pressure; then the pressure jumped abruptly as additional liquid was forced into an already full cell. Continued injection allowed the liquid compressibility to be determined as far as the highest gage pressure: 6 MPa (for comparison, note that the greatest pressure for vibrating densitometry is 35 MPa). The intersection of the steep and flat portions of the (n, p) curve specified the liquid-phase molar volume at the equilibrium vapor pressure.

For vapor-pressure measurements the cell was two-thirds filled near room temperature, isolated from the screw injector, and pressure was measured at suitable intervals up to the critical temperature. Critical temperatures T^c were measured by visually determining the loss of meniscus in sealed capillaries; critical pressures were then obtained by extrapolating the vapor pressure against temperature curves to T^c. Freezing temperatures were determined by observing solidification in sealed capillaries but the measurements were in a region with poor temperature control and are reliable to no better than 1 K. Boiling temperatures for all compounds except $CFCl_3$ (R11) are well below room temperature and also lie in a region where we had poor temperature control. For these compounds the boiling temperatures were estimated by following the (p, T) curves for $(0.06 < p/\text{MPa} < 0.13)$ as the samples warmed rapidly. Since equilibrium was not established, the results can be used to locate T^b only approximately: our estimate of the uncertainty is $\pm(1$ to $2)$ K. We are currently employed in extending high-precision measurements to the range $(230 < T/\text{K} < 300)$ and shall report more accurate measurements in this region in a subsequent paper. Our present interest, however, focuses on results from room temperature to the critical region. For $CFCl_3$, T^b was determined from the fit to the high-precision vapor pressures and agrees within 0.01 K with recommended values.[12]

The present values for the critical temperatures are also relatively crude and the temperature of meniscus disappearance is established only within about 0.3 K. Vapor pressures and liquid and vapor densities are reported at much higher precision. For those experiments, temperature measurement and control was ± 1 mK. Pressure measurements in the (p, V_m, T) apparatus of Kooner and Van Hook[7] were established to ± 0.01 per cent of full scale (6 MPa), and to about ± 0.01 MPa for vibrating densitometry.

3. Results

Melting (T^m), boiling (T^b), and critical (T^c) temperatures, and critical pressure (p^c) and molar volumes (V_m^c) are reported in table 2 where they are compared (as appropriate) with the literature values. The agreement is within the experimental uncertainties discussed above. T^m, T^b, and T^c were measured as described above, p^c was obtained by combining T^c with equation (2), and V_m^c from T^c and the law of rectilinear diameters as described in the text surrounding equation (10).

Vapor pressures p^σ for the title compounds are reported in table 3. They were

TABLE 2. Transition temperatures and critical properties of the title compounds. M is molar mass

	M / g·mol⁻¹	$T^{m\,a}$ / K	$T^{b\,a}$ / K	$T^{c\,b}$ / K	$p^{c\,c}$ / MPa	$10^6 · V_m^{c\,d}$ / m³·mol⁻¹
CFCl₃ "R11"	137.37	162	296.79	471.1	4.466	$246._8$
		162[21]	296.78[12,19]	471.15[21]	4.474[12]	248.1[12]
CF₂ClH "R22"	86.47	114	232.40	369.5	5.035	$164._3$
		113[21]	232.33[12]	369.3[21]	5.033[12]	164.8[12]
CF₃OCF₂OCF₃	220.02	112	263	372.3_5	2.333	363
CF₃OCF₂CF₂H	186.03	132	270	387.7_5	2.640	337
c-CF₂CF₂CF₂O	166.02	156	244	361.8_5	3.094	272
CF₃OCF₂H	136.02	116	237	353.8_5	3.326	e
		117[21]	238[20]			
CF₃OCH₃	100.04	124	249	378.0_5	3.680	228
			250[20]			

[a] This work except as noted, (± 1 K).
[b] This work except as noted, (± 0.1 K).
[c] Calculated from T^c, equation (3), and table 4.
[d] This work except as noted. Calculated from equation (9).
[e] Insufficient sample available to complete this measurement.

smoothed by least-squares fitting to the equations (both forms are commonly used):

$$\ln(p^\sigma/\text{Pa}) = A_0 + A_1 · (\text{K}/T) + A_2 · (T/\text{K}) + A_3 · \ln(T/\text{K}), \qquad (2)$$

$$\ln(p^\sigma/\text{Pa}) = \ln(p^c/\text{Pa}) + (T^c/T) · \{\textstyle\sum_i A_i' · (1 - T/T^c)^i\}. \qquad (3)$$

The derived parameters and variances are reported in table 4. The present measurements lie about 0.4 per cent below values calculated from the ASHRAE (American Society for Heating Refrigeration and Air Conditioning Engineers) smoothing equation[12] for CFCl₃ (R11) for ($303 < T/\text{K} < 463$; $0.643 < T/T^c < 0.983$) and about 0.2 per cent above the ASHRAE values[12] for CF₂ClH (R22) for ($303 < T/\text{K} < 363$, or $< 0.821 < T/T^c < 0.984$), indicating good consistency between our pressure and temperature calibrations and those of other laboratories.

Densities obtained from vibrating densitometry on the liquids at approximately 10 K and 5 MPa intervals over the range ($303 < T/\text{K} < 373$ or $T/T^c < 0.92$, whichever is lower; and $0.1 < p/\text{MPa} < 35$) were smoothed by least-squares fitting with the equation:

$$\begin{aligned}
\ln\{10^{-3} · \rho/(\text{kg}·\text{m}^{-3})\} = {}& \ln\{10^{-3} · \rho_o/(\text{kg}·\text{m}^{-3})\} + \{\alpha_0 · (t/\text{K}) + (1/2)\alpha_1 · (t/\text{K})^2 \\
& + (1/3)\alpha_2 · (t/\text{K})^3\} + \textstyle\sum_{i=1}^{3} \{\kappa_{i,0} + \kappa_{i,1} · (t/\text{K}) \\
& + \kappa_{i,2} · (t/\text{K})^2\} · (p/\text{MPa})^i/i. \qquad (4)
\end{aligned}$$

Parameters and variances of fit are reported in table 5. Here ρ_o is the hypothetical reference density at $T = 273.15$ K and $p = 0$ and $t = (T - 273.15$ K). The thermal expansivity α and isothermal compressibility κ were obtained by appropriate differentiation:

$$-\alpha/\text{K}^{-1} = \{\alpha_0 + \alpha_1 · (t/\text{K}) + \alpha_2 · (t/\text{K})^2\} + \textstyle\sum_{i=1}^{3} (\kappa_{i,1} + 2\kappa_{i,2} · (t/\text{K})\} · (p/\text{MPa})^i/i, \qquad (5)$$

$$\kappa/\text{GPa}^{-1} = \textstyle\sum_{i=1}^{3} \{\kappa_{i,0} + \kappa_{i,1} · (t/\text{K}) + \kappa_{i,2} · (t/\text{K})^2\} · (p/\text{MPa})^{i-1}. \qquad (6)$$

TABLE 3. Vapor pressures p^σ of the title compounds

CFCl$_3$ (R11)		CF$_2$ClH (R22)		CF$_3$OCF$_2$OCF$_3$		CF$_3$OCF$_2$CF$_2$H	
T/K	$\ln(p^\sigma$/Pa)	T/K	$\ln(p^\sigma$/Pa)	T/K	$\ln(p^\sigma$/Pa)	T/K	$\ln(p^\sigma$/Pa)
304.248	11.78555	303.110	14.00183	303.467	12.96839	303.626	12.74291
310.439	11.98841	309.202	14.15530	307.193	13.07767	308.556	12.89479
316.831	12.18857	311.382	14.21003	311.232	13.19429	313.672	13.04669
325.919	12.45742	315.854	14.32004	315.057	13.30221	317.519	13.15755
335.243	12.71587	319.734	14.41078	318.886	13.40677	321.351	13.26448
344.783	12.96448	323.089	14.49078	322.789	13.51078	325.307	13.37236
354.579	13.20569	328.017	14.55515	326.727	13.61381	329.258	13.47756
364.471	13.43249	329.979	14.64350	330.760	13.71637	333.214	13.57966
374.586	13.65539	333.965	14.72958	334.727	13.81443	337.264	13.68211
385.212	13.87357	338.047	14.81870	338.789	13.91405	341.360	13.78293
396.033	14.08422	342.133	14.90195	342.897	14.01121	345.460	13.88113
407.184	14.28966	346.224	14.98558	346.989	14.10729	349.616	13.97895
418.690	14.49180	350.421	15.08934	351.267	14.20517	353.837	14.07574
430.460	14.68870	353.192	15.12406	355.501	14.29962	358.124	14.17171
439.055	14.82847	356.025	15.17980	358.356	14.36297	362.134	14.25996
447.950	14.96625	358.809	15.22992	360.921	14.41951	366.502	14.35396
456.867	15.09937	361.659	15.28792	363.751	14.47933	370.917	14.44694
462.322	15.18039	364.570	15.34331	366.523	14.53906	375.327	14.53783
466.140	15.23982	366.057	15.37137	368.193	14.57571	379.905	14.63084
468.014	15.26724	367.535	15.39900	369.458	14.60114	384.449	14.72146
469.868	15.29598	368.962	15.42583	370.937	14.63432	385.975	14.75189

c-CF$_2$CF$_2$CF$_2$O		CF$_3$OCF$_2$H		CF$_3$OCH$_3$	
T/K	$\ln(p^\sigma$/Pa)	T/K	$\ln(p^\sigma$/Pa)	T/K	$\ln(p^\sigma$/Pa)
303.676	13.60578	303.388	13.84334	303.636	13.43163
307.353	13.70490	305.842	13.90836	306.786	13.51896
311.153	13.80474	308.337	13.97328	310.576	13.62120
314.957	13.90248	310.874	14.03859	314.419	13.72274
318.776	13.99790	313.423	14.10292	318.198	13.81954
322.669	14.09286	315.974	14.16660	322.100	13.91776
326.627	14.18726	318.497	14.22869	326.037	14.01400
330.620	14.27985	321.092	14.29114	329.959	14.10768
334.577	14.36990	323.728	14.35391	333.995	14.20212
338.669	14.46071	326.357	14.41539	338.057	14.29458
342.887	14.55281	328.998	14.47656	342.113	14.38516
346.949	14.63951	331.611	14.53606	346.245	14.47552
351.157	14.72757	334.286	14.59623	350.452	14.56559
355.390	14.81482	337.023	14.65694	354.684	14.65412
359.417	14.89595	339.753	14.71685	358.690	14.73664
		342.485	14.77623	363.044	14.82457
		345.199	14.83475	367.403	14.91146
		347.985	14.89370	370.349	14.96964
		350.794	14.95360	373.268	15.02613
		352.194	14.98274	374.738	15.05523
		353.605	15.01229	376.280	15.08506

Liquid densities ρ, molar volumes V_m, compressibilities κ, and expansivities α along the saturated vapour-pressure curve calculated from equations (2), (4), (5), and (6) are reported at round temperatures in table 6 and compared with the literature values for CFCl$_3$ and CF$_2$ClH.[12, 13] The agreement for the densities is almost always within ± 2 kg·m^{-3} (± 0.15 per cent), roughly three to five times the internal

TABLE 4. The parameters of equations (2) and (3). Least-squares fits of the results in table 3

(a) equation (2): $\ln(p^\sigma/Pa) = A_0 + A_1 \cdot (K/T) + A_2 \cdot (T/K) + A_3 \cdot \ln(T/K)$					
Compound	A_0	$-A_1$	$10^2 \cdot A_2$	$-A_3$	$10^7 \cdot \sigma^2$
$CFCl_3$ (R11)	137.5388	6679.053	2.568621	19.52070	21
CF_2ClH (R22)	253.3180	8821.011	6.249096	40.10385	5.2
$CF_3OCF_2OCF_3$	245.5559	8991.460	5.994252	38.69449	3.8
$CF_3OCF_2CF_2H$	202.4236	8114.230	4.523931	30.91298	0.4
$c\text{-}CF_2CF_2CF_2O$	227.1457	8218.118	5.538288	35.56644	0.2
CF_3OCF_2H	327.0939	10776.04	8.478943	53.09804	0.4
CF_3OCH_3	224.5174	8253.781	5.398848	35.04229	1.0

(b). equation (3): $\ln(p^\sigma/Pa) = \ln(p^c/Pa) + (T^c/T) \cdot \{\sum_{i=1}^{3} A_i' \cdot (1 - T/T^c)^i\}$					
Compound	$\ln(p_c/Pa)$	$-A_1'$	A_2'	$-A_3'$	$10^7 \cdot \sigma^2$
$CFCl_3$ (R11)	15.31189	6.794222	2.793550	4.973385	17
CF_2ClH (R22)	15.43191	6.857625	3.210181	8.153974	5.0
$CF_3OCF_2OCF_3$	14.66267	7.781435	3.167311	7.933039	3.7
$CF_3OCF_2CF_2H$	14.78833	7.566167	2.303828	6.570587	0.3
$c\text{-}CF_2CF_2CF_2O$	14.94485	7.199994	2.500954	7.464408	0.2
CF_3OCF_2H	15.01731	7.363544	3.605178	10.35180	0.4
CF_3OCH_3	15.11842	7.210882	3.101386	7.312956	0.8

precision calculated from the variances in tables 4 and 5. This is reasonable in view of the different forms of the smoothing relations used by us and other authors and, more importantly, because of the necessity of controlling both temperature and pressure in a region where thermal pressure fluctuations introduce significant corrections to the density. We can find no apparent reason to favor either the present or the literature results and conclude that the densities reported for the title compounds are accurate to ± 0.1 per cent or better for $(303 < T/K < 373)$. The compressibilities and expansivities are also in good agreement with the ASHRAE[12] values. The proliferation of parameters in the ASHRAE smoothing relations makes them susceptible to polynomial ripple; this might exacerbate statistical error for differential properties such as compressibility and expansivity and account for some of the differences.

The vapor-density measurements obtained from the Kooner–van Hook (KVH) (p, V_m, T) apparatus are of useful precision only for $(0.3 < p/MPa < p^\sigma)$. At each temperature a least-squares fit to the equation:

$$p^{-1} \cdot [\{pV_{cell}/(n_{inj}RT)\} - 1] = B_{vap} + C_{vap} \cdot p, \tag{7}$$

with either one or two parameters as determined from the F-ratio at 90 per cent confidence is reported in table 7. Trials with an additional term $D_{vap} \cdot p^2$ showed no improvement in the statistical quality of fit. Reference second virial coefficients B are available for CCl_3F (R11)[9,14,16] and CF_2ClH (R22).[16,17] These literature values, which report B only, are in good agreement with each other but lie significantly above the present values of B_{vap}. We ascribe the differences to a number of causes. To begin with, the earlier studies[14,17] all restricted themselves to the low-pressure regime, $p < 0.07$ MPa, where the contribution of $C_{vap} \cdot p$ and higher terms can be

TABLE 5. The parameters of equation (4). Densities of title compounds by vibrating densitometry.

$$\ln\{10^{-3}\cdot\rho/(kg\cdot m^{-3})\} = \ln\{10^{-3}\cdot\rho_o/(kg\cdot m^{-3})\} + \{\alpha_0\cdot(t/K)+(1/2)\cdot\alpha_1\cdot(t/K)^2+(1/3)\cdot\alpha_2\cdot(t/K)^3$$
$$+\sum_{i=1}^{3}\{\kappa_{i,0}+\kappa_{i,1}\cdot(t/K)+\kappa_{i,2}\cdot(t/K)^2\}\cdot(p/MPa)^i/i$$

	$CFCl_3$ (R11)	CF_2ClH (R22)	$CF_3OCF_2OCF_3$	$CF_3OCF_2CF_2H$
$\ln\{(\rho_o/(kg\cdot m^{-3}))\}$	0.4253234	0.2184011	0.3935191	0.4198042
α_0	$-1.457188\cdot10^{-3}$	$-9.842254\cdot10^{-4}$	a	$-2.829941\cdot10^{-3}$
α_1	$-3.675199\cdot10^{-6}$	$-8.603401\cdot10^{-5}$	$-1.329373\cdot10^{-4}$	a
α_2	$-6.667333\cdot10^{-8}$	a	$8.218383\cdot10^{-7}$	$-2.782478\cdot10^{-7}$
$\kappa_{1,0}$	$1.629408\cdot10^{-3}$	$4.817711\cdot10^{-3}$	$2.707804\cdot10^{-3}$	$1.661375\cdot10^{-3}$
$\kappa_{1,1}$	$1.214335\cdot10^{-6}$	$-7.753518\cdot10^{-5}$	$9.397306\cdot10^{-5}$	$6.358145\cdot10^{-5}$
$\kappa_{1,2}$	$2.984636\cdot10^{-7}$	$3.571970\cdot10^{-6}$	$1.776659\cdot10^{-6}$	$1.196005\cdot10^{-6}$
$\kappa_{2,0}$	$-2.078216\cdot10^{-5}$	$-1.039304\cdot10^{-4}$	a	$1.778933\cdot10^{-4}$
$\kappa_{2,1}$	a	$3.054207\cdot10^{-6}$	$-7.190825\cdot10^{-6}$	$-9.133276\cdot10^{-6}$
$\kappa_{2,2}$	$-1.328092\cdot10^{-8}$	$-2.126743\cdot10^{-7}$	$-1.250993\cdot10^{-7}$	$-4.143482\cdot10^{-8}$
$\kappa_{3,0}$	a	a	a	$-6.427716\cdot10^{-6}$
$\kappa_{3,1}$	$5.268571\cdot10^{-9}$	a	$1.145995\cdot10^{-7}$	$2.632991\cdot10^{-7}$
$\kappa_{3,2}$	$1.606324\cdot10^{-10}$	$3.285200\cdot10^{-9}$	$2.651731\cdot10^{-9}$	a
$10^6\cdot\sigma^2$	0.02	0.8	3.0	3.6
T/K	303 to 375	303 to 344	303 to 346	303 to 364
p/MPa	0.3 to 35	0.3 to 35	0.3 to 35	0.3 to 35

	$c\text{-}CF_2CF_2CF_2O$	CF_3OCF_2H	CF_3OCH_3
$\ln\{\rho_o/(kg\cdot m^{-3})\}$	0.407265	0.285874	0.143788
α_0	$-3.070092\cdot10^{-3}$	a	$-1.590875\cdot10^{-3}$
α_1	$-4.378789\cdot10^{-5}$	$-1.893692\cdot10^{-4}$	$-5.502974\cdot10^{-5}$
α_2	a	$1.439419\cdot10^{-6}$	a
$\kappa_{1,0}$	a	$2.750260\cdot10^{-3}$	$3.672450\cdot10^{-3}$
$\kappa_{1,1}$	$2.420665\cdot10^{-4}$	$1.789850\cdot10^{-4}$	a
$\kappa_{1,2}$	$6.586677\cdot10^{-7}$	$1.323963\cdot10^{-6}$	$2.122383\cdot10^{-6}$
$\kappa_{2,0}$	$2.462225\cdot10^{-4}$	a	a
$\kappa_{2,1}$	$-2.088783\cdot10^{-5}$	$-1.5445527\cdot10^{-5}$	$-3.353513\cdot10^{-6}$
$\kappa_{2,2}$	a	$-3.038526\cdot10^{-8}$	$-1.071273\cdot10^{-7}$
$\kappa_{3,0}$	$-4.684476\cdot10^{-6}$	a	$-2.563132\cdot10^{-6}$
$\kappa_{3,1}$	$3.851825\cdot10^{-7}$	$3.008145\cdot10^{-7}$	$1.417130\cdot10^{-7}$
$\kappa_{3,2}$	a	a	$1.205022\cdot10^{-9}$
$10^6\cdot\sigma^2$	3.2	2.8	3.0
T/K	303 to 337	303 to 344	303 to 359
p/MPa	0.3 to 35	0.3 to 35	0.3 to 35

^{a} This parameter set to zero in least-squares routine.

ignored. The present results, on the other hand, are at much higher pressures: $0.3 < p/MPa < 4$, where the higher-order terms do make important contributions. Because the present results do not extend into the low-pressure region with useful precision, they cannot be used to obtain a properly extrapolated value for B. Inside our pressure range, errors thus introduced are least-squares compensated by an adjusted value for C_{vap} and there is a large correlation term in the statistical error matrix associated with the parameters. This can be demonstrated in a number of ways. Thus, when we fit the present values to equation (7), but without the $C_{vap}\cdot p$ term, the derived values for B_{vap} are then in much better agreement with the references,[14-17] even though the statistical quality of fit to the present higher-pressure values declines. Alternatively, by fitting to equation (7) using terms as high

TABLE 6. Properties of the saturated liquid at round temperatures from equations (2), (4), (5), and (6);[a] or equations (2), (11), and (12).[b] Parenthesized values quoted from reference 12

Compound	$\dfrac{T}{K}$	$\dfrac{p}{MPa}$	$\dfrac{\rho}{kg \cdot m^{-3}}$	$\dfrac{10^6 \cdot V_m}{m^3 \cdot mol^{-1}}$	$\dfrac{\alpha}{kK^{-1}}$	$\dfrac{\kappa}{GPa^{-1}}$
CCl_3F (R11)	303.15[a]	0.1265 (0.1270)	1462 (1464)	93.98	1.63	1.93
	323.15[a]	0.2375 (0.2377)	1413 (1415)	97.22	1.80	2.43
	343.15[a]	0.4100 (0.4106)	1361 (1363)	101.0	2.02	3.16
	363.15[a]	0.6625 (0.6648)	1305 (1306)	105.3	2.29	4.10
	383.15[b]	1.0157 (1.0215)	$1.24 \cdot 10^3$ (1244)	111		5.1
	403.15[b]	1.4931 (1.5042)	$1.17 \cdot 10^3$ (1174)	117		8.4
	423.15[b]	2.1221 (2.1390)	$1.09 \cdot 10^3$ (1092)	126		14
	443.15[b]	2.9359 (2.9558)	974 (989)	141		32
	463.15[b]	3.9744 (3.9896)	833 (818)	165		118
	468.15[b]	4.2747 (4.2870)	789	174		196
CF_2ClH (R22)	303.15[a]	1.2047 (1.2012)	1170 (1171)	73.91	3.41	5.47
	323.15[a]	1.9636 (1.9579)	1083 (1082)	79.81	4.77	8.95
	343.15[a]	3.0261 (3.0206)	986 (970)	87.64	5.85	14.2
	353.15[b]	3.6990 (3.6928)	926 (894)	93.4		44
	363.15[b]	4.4862 (4.4800)	823 (781)	105		123
$CF_3OCF_2OCF_3$	303.15[a]	0.4243	1411	156.0	3.17	6.99
	323.15[a]	0.7446	1310	167.9	4.40	11.4
	343.15[a]	1.2239	1201	183.2	4.88	16.7
	353.15[b]	1.5402	$1.11 \cdot 10^3$	198		39
	363.15[b]	1.9194	$1.02 \cdot 10^3$	215		66
	368.15[b]	2.1358	969	227		91
$CF_3OCF_2CF_2H$	303.15[a]	0.3370	1396	133.2	3.04	4.60
	323.15[a]	0.6057	1312	141.8	3.42	7.60
	343.15[a]	1.0106	1223	152.1	3.97	11.3
	363.15[a]	1.5943	1131	164.4	4.66	15.6
	373.15[b]	1.9696	$1.05 \cdot 10^3$	177		47
	383.15[b]	2.4115	969	192		87
$c\text{-}C_2F_5CF_2O$	303.15[a]	0.7991	1350	122.96	4.26	4.18
	323.15[a]	1.3349	1229	135.08	5.28	
	333.15[a]	1.6856	1159	143.37		
	343.15[b]	2.1022				
	353.15[b]	2.5941				
	358.15[b]	2.8720				
CF_3OCF_2H	303.15[a]	1.0213	1250	108.85	4.13	8.82
	323.15[a]	1.6897	1143	119.04	5.37	13.6
	343.15[a]	2.6521	1041	130.68		
	348.15[b]	2.9511				
	353.15[b]	3.2779				
CF_3OCH_3	303.15[a]	0.6718	1078	92.82	3.16	5.45
	323.15[a]	1.1368	1005	99.52	4.11	8.49
	343.15[a]	1.8082	924.8	108.18	4.93	12.7
	353.15[a]	2.2404	884.0	113.12		
	363.15[b]	2.7502				
	373.15[b]	3.3493				

as $D_{vap} \cdot p^2$, but with B_{vap} fixed to the low-pressure literature values, one finds about the same statistical quality as for the earlier two-parameter unconstrained fits (table 7). However, this is not useful for the fluorinated ethers, the compounds of principal interest in this paper. Low-pressure B_{vap}s are not available for them. In any case, direct comparisons of B_{vap}s extracted from information for widely different

TABLE 7. Least-squares parameters of equations (7)[a] and (8)

Compound	$\frac{T}{K}$	$\frac{-B_{vap}}{MPa^{-1}}$	$\frac{C_{vap}}{MPa^{-2}}$	$10^3 \cdot \sigma^2$	$\ln\{\frac{V_m^\sigma}{(m^3 \cdot mol^{-1})}\}$	$-\kappa_0$	$-\kappa_1$	$10^8 \cdot \sigma^2$
CCl_3F	343.33	3.547	5.650	1.9	-9.2009	$-2.71 \cdot 10^{-3}$	$6.92 \cdot 10^{-5}$	0.1
	362.83	1.960	2.121	1.3	-9.1584	$-3.17 \cdot 10^{-3}$		0.8
	382.57	1.273	0.9858	2.3	-9.1089	$-5.07 \cdot 10^{-3}$	$1.23 \cdot 10^{-4}$	0.7
	402.72	0.7675	0.4068	1.9	-9.0489	$-8.22 \cdot 10^{-3}$	$3.30 \cdot 10^{-4}$	0.8
	423.78	0.4385	0.1396	1.4	-8.9718	$-1.46 \cdot 10^{-2}$	$8.63 \cdot 10^{-4}$	1.7
	441.06	0.2991	0.0637	1.0	-8.8863	$-2.88 \cdot 10^{-2}$	$2.84 \cdot 10^{-3}$	4.5
	455.97	0.1446		3.1	-8.7795	$-6.47 \cdot 10^{-2}$	$1.08 \cdot 10^{-2}$	35
	463.07	0.1273		0.6	-8.7002	-0.1229	$3.19 \cdot 10^{-2}$	350
	466.62	0.1479^b		0.9	-8.6793	-0.1580	$4.76 \cdot 10^{-2}$	270
	470.44	0.1412		0.8	-8.6030	-0.2990	0.1478	1850
CF_2ClH	306.89	0.2357^b		1.6	-9.4922	$-4.70 \cdot 10^{-3}$		0.9
	311.96	0.2833		0.4	-9.4811	$-5.47 \cdot 10^{-3}$		5.7
	322.19	0.2410		0.2	-9.4375	$-8.77 \cdot 10^{-3}$	$2.49 \cdot 10^{-4}$	2.6
	333.32	0.4038	0.0979	0.1	-9.3888	$-1.22 \cdot 10^{-2}$		180
	342.87	0.3424	0.0674	0.3	-9.3342	$-2.29 \cdot 10^{-2}$	$2.11 \cdot 10^{-3}$	5.1
	353.98	0.3502	0.0612	1.2	-9.2708	$-4.42 \cdot 10^{-2}$	$6.31 \cdot 10^{-3}$	3.3
	363.77	0.3114	0.0480	0.9	-9.1659	-0.1364	$4.92 \cdot 10^{-2}$	280
	366.66	0.3146^b	0.0489	0.9	-9.0643	-0.2596	0.1504	310
	368.14	0.3074^b	0.0448	1.2	-9.0148	-0.4155	0.3240	1450
$CF_3OCF_2OCF_3$	312.55	0.5915		2.5	-8.7256	$-8.24 \cdot 10^{-3}$	$2.31 \cdot 10^{-4}$	3.3
	322.80	0.5253		1.9	-8.6865	$-1.15 \cdot 10^{-2}$	$4.64 \cdot 10^{-4}$	22
	333.36	0.8589	0.4557	3.2	-8.6437	$-1.63 \cdot 10^{-2}$	$8.30 \cdot 10^{-4}$	8.7
	342.87	0.9167	0.4959	5.3	-8.5934	$-2.58 \cdot 10^{-2}$	$1.85 \cdot 10^{-3}$	275
	354.03	0.9617	0.5051	7.6	-8.5206	$-4.13 \cdot 10^{-2}$	$3.76 \cdot 10^{-3}$	76
	362.13	0.5662	0.1924	0.3	-8.4541	$-6.06 \cdot 10^{-2}$	$6.51 \cdot 10^{-3}$	250
	366.54	0.5778	0.1889	0.5	-8.4116	$-8.06 \cdot 10^{-2}$	$1.01 \cdot 10^{-2}$	450
	369.46	0.6162^b	0.1613	15	-8.3728	-0.1022	$1.45 \cdot 10^{-2}$	1200
$CF_3OCF_2CF_2H$	313.67	1.2567^b		2.0	-8.8891	$-5.35 \cdot 10^{-3}$	$1.77 \cdot 10^{-4}$	2.0
	323.99	2.0352	1.847	6.6	-8.8647	$-6.92 \cdot 10^{-3}$		3.3
	333.24	2.2433	2.061	13	-8.8400	$-9.32 \cdot 10^{-3}$	$1.90 \cdot 10^{-4}$	2.5
	342.77	1.8589	1.476	4.2	-8.8089	$-1.26 \cdot 10^{-2}$	$4.76 \cdot 10^{-4}$	1.0
	353.90	1.7702	1.207	15	-8.7615	$-1.85 \cdot 10^{-2}$	$9.98 \cdot 10^{-4}$	5.1
	363.65	1.3294	0.760	2.0	-8.7106	$-2.83 \cdot 10^{-2}$	$2.30 \cdot 10^{-3}$	22
	372.49	1.1265	0.559	1.7	-8.6498	$-4.30 \cdot 10^{-2}$	$4.30 \cdot 10^{-3}$	70
	378.57	0.8348^b	0.305	1.3	-8.5965	$-6.59 \cdot 10^{-2}$	$8.50 \cdot 10^{-3}$	480
	383.05	0.8730	0.326	2.2	-8.5440	$-9.49 \cdot 10^{-2}$	$1.45 \cdot 10^{-2}$	1900
	386.10	0.9315	0.358	3.7	-8.5156	-0.1069	$1.69 \cdot 10^{-2}$	1500
$c\text{-}CF_2CF_2CF_2O$	313.14	0.2518		15	-8.9554	$-1.07 \cdot 10^{-2}$	$9.58 \cdot 10^{-4}$	1.4
	323.43	0.2226		6.0	-8.9046	$-1.54 \cdot 10^{-2}$	$1.38 \cdot 10^{-3}$	1.5
	334.04	0.1814		2.6	-8.8432	$-2.30 \cdot 10^{-2}$	$2.23 \cdot 10^{-3}$	2.7
	343.49	0.1694		0.8	-8.7716	$-3.85 \cdot 10^{-2}$	$4.39 \cdot 10^{-3}$	29
	349.07	0.1051	-0.0386	0.1	-8.7188	$-5.71 \cdot 10^{-2}$	$7.72 \cdot 10^{-3}$	131
	353.29	0.0891	-0.0388	0.1	-8.6594	$-8.82 \cdot 10^{-2}$	$1.41 \cdot 10^{-2}$	198
	357.28	0.1218	-0.0197	0.1	-8.6110	-0.1142	$2.05 \cdot 10^{-2}$	163
	360.14	0.0684	-0.0387	0.1	-8.5591	-0.1444	$2.81 \cdot 10^{-2}$	311
CF_3OCH_3	323.43	0.3645		1.0	-9.2026	$-8.74 \cdot 10^{-3}$	$3.91 \cdot 10^{-4}$	2.3
	334.03	0.3030		1.2	-9.1558	$-1.22 \cdot 10^{-2}$	$5.45 \cdot 10^{-4}$	5.3
	343.49	0.2349		1.4	-9.1065	$-1.76 \cdot 10^{-2}$	$1.04 \cdot 10^{-3}$	4.2
	353.28	0.1931		0.6	-9.0457	$-2.74 \cdot 10^{-2}$	$2.08 \cdot 10^{-3}$	17
	363.06	0.1738		0.5	-8.9635	$-4.84 \cdot 10^{-2}$	$5.30 \cdot 10^{-3}$	63
	367.43	0.1566		0.5	-8.9151	$-6.79 \cdot 10^{-2}$	$9.16 \cdot 10^{-3}$	176
	373.27	0.1384		0.2	-8.8340	-0.1112	$1.95 \cdot 10^{-2}$	898
	376.31	0.1345		0.1	-8.7841	-0.1476	$2.90 \cdot 10^{-2}$	2080

[a] Pressure range for vapor phase fits to equation (7) is $0.3 \leqslant p/MPa \leqslant p^\sigma$.
[b] Excluded from least squares for equation (10).

pressure ranges are inappropriate. We conclude that the B_{vap} and C_{vap} parameters given in table 7, and taken as pairs, accurately describe vapor non-ideality for the compounds investigated, but only over the pressure range indicated in the table.

Liquid molar volumes obtained in the KVH (p, V_m, T) apparatus were least-squares smoothed with the equation:

$$\ln\{V_m/(m^3 \cdot mol^{-1})\} = \ln\{(V_{cell}/n_{inj})/(m^3 \cdot mol^{-1})\}$$
$$= \ln\{V_m^\sigma/(m^3 \cdot mol^{-1})\} - \kappa_0 \cdot \{(p-p^\sigma)/MPa\}$$
$$- \kappa_1 \cdot \{(p-p^\sigma)/MPa\}^2. \qquad (8)$$

The parameters and variances of fit are reported in table 7. As for the vapor, either two or three parameters were used according to the F-ratio test at 90 per cent confidence. In equation (8), V_m^σ is the orthobaric molar volume, p^σ is the vapor pressure, and κ_0 and κ_1 are constants related to the zeroth- and first-order compressibility coefficients:

$$\kappa/GPa^{-1} = \kappa_0 + 2\kappa_1 \cdot \{(p-p^\sigma)/MPa\} + \ldots. \qquad (9)$$

Orthobaric vapor and liquid volumes at the experimental temperatures as obtained from the parameters of table 7 were used to calculate orthobaric liquid and vapor densities. These were in turn least-squares fitted to the law of rectilinear diameters:[18]

$$(1/2)(\rho_{liq}^\sigma + \rho_{vap}^\sigma)/(kg \cdot m^{-3}) = (M/2)\{(1/V_{liq}^\sigma) + (1/V_{vap}^\sigma)\}/(kg \cdot m^{-3})$$
$$= D_0 + D_1 \cdot (T^c - T)/K, \qquad (10)$$

to obtain the critical density from the measurement of T^c. The parameters D_0 and D_1 are reported in table 8; M is the molar mass. The corresponding critical volumes have been reported in table 2.

TABLE 8. The parameters of equations (10), (11), and (12)

	CCl_3F	CF_2ClH	$CF_3OCF_2OCF_3$	$CF_3OCF_2CF_2H$	$c\text{-}CF_2CF_2CF_2O$	CF_3OCF_2H	CF_3OCH_3
D_0	556.7	526.4	606.9	552.4	610.1	a	437.9
D_1	1.120	1.522	1.881	2.599	1.551		1.854
σ^2	190	48	52	97	24		53
β	1/7	1/7	1/6	1/6	1/6	a	1/6
E_0	3810	3246	3838	5612	4185		5835
E_1	-9900	$3.288 \cdot 10^4$	-7276	$-1.449 \cdot 10^4$	$-1.201 \cdot 10^4$		$-1.553 \cdot 10^4$
E_2	$7.485 \cdot 10^4$	$-8.876 \cdot 10^4$	$4.048 \cdot 10^4$	$6.193 \cdot 10^4$	$8.576 \cdot 10^4$		$1.052 \cdot 10^5$
E_3	$-8.990 \cdot 10^4$	$1.095 \cdot 10^5$	$-4.236 \cdot 10^4$	$-6.468 \cdot 10^4$	$-1.148 \cdot 10^5$		$-1.346 \cdot 10^5$
σ^2	$5 \cdot 10^{-4}$	$8 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$2 \cdot 10^{-4}$		$1 \cdot 10^{-4}$
F_0	3.0381	9.7440	2.6194	2.1509	1.0678	a	2.6861
F_1	51.212	14.065	19.856	25.737	43.033		32.535
F_2	-296.5	-26.851	-28.733	-52.713	-144.52		-92.078
F_3	681.4	b	b	b	b		b
F_{const}	b	-3.4564	0.9029	1.1458	1.3235		0.5815
β	1/7	1/7	1/7	1/7	1/7		1/7
σ^2	$1.7 \cdot 10^{-3}$	$4.4 \cdot 10^{-3}$	$0.9 \cdot 10^{-3}$	$3.6 \cdot 10^{-3}$	$3.6 \cdot 10^{-3}$		$1.0 \cdot 10^{-3}$

a Insufficient sample for these measurements.

b This parameter set to zero in least-squares routine.

Even further smoothing is useful. The orthobaric molar volumes at experimental temperatures above 323 K (table 7) were empirically smoothed using the equation:

$$\ln[\{(1/V_m^\sigma) - (1/V_m^c)\}/(\text{mol}\cdot\text{m}^{-3})] = \ln(\sum_{i=0}^{3} E_i\phi^{(i/2+\beta)}). \tag{11}$$

which focuses attention on the high-temperature liquid in the region approaching T^c, and where ϕ is the reduced temperature: $\phi = (T^c - T)/T^c$, the E_is are least-squares fitting parameters, and β is an empirically selected exponent. No special significance beyond statistical convenience is attributed to the value of β selected for equations (11) and (12). The parameters of fit to equation (11) are reported in table 8. For the liquid-phase compressibilities under orthobaric conditions we proceeded by recognizing that κ becomes large at T^c and therefore chose to least-squares fit logarithmic reciprocal compressibilities in the high-temperature region with the equation:

$$\ln(\text{GPa}^{-1}/\kappa^\sigma) = \sum_{i=0}^{3} F_i\phi^{(i+\beta)} + F_{\text{const}}. \tag{12}$$

Logarithmic functions have been introduced in equations (11) and (12) in order to insure smooth weighting across the entire range of results. The results are reported in table 8. The F_is are least-squares parameters. Expansivities in the high-temperature region under orthobaric or isobaric conditions can be readily calculated by making the appropriate substitutions in equations (8), (11), and (12).

4. Discussion

Results have been presented in a form convenient for thermodynamic calculations, including work/heat refrigeration cycles. We are presently engaged in synthesizing other fluorinated and partially fluorinated ethers and in measuring their thermodynamic properties. Once these results become available we hope to generate a description of the dependence of various thermodynamic properties on fluorine content and molecular structure.

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