

Thermodynamic properties of CFC alternatives: A survey of the available data*

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The thermodynamic properties of ten halogenated hydrocarbons are collected from a variety of sources, including unpublished data. Considered are the triple point, normal boiling point and critical point parameters, and the temperature dependence of the vapour pressure, saturated liquid density and ideal gas heat capacity. Also considered are the single-phase p - V - T data. The saturation and ideal gas data are fitted to simple correlations. The fluids, which are potential alternatives to the fully halogenated chlorofluorocarbons, are R23, R32, R125, R143a, R22, R134a, R152a, R124, R142b and R123.

(Keywords: thermodynamic properties; alternative refrigerants, CFCs)

Propriétés thermodynamiques de substituts de CFC: Synthèse des données disponibles

Les propriétés thermodynamiques de dix hydrocarbures halogénés ont été recueillies à partir de plusieurs sources, et notamment des données non publiées à ce jour. On considère le point triple, le point d'ébullition normal et les paramètres du point critique ainsi que la dépendance de température de la pression de vapeur, la densité de liquide saturé et la capacité calorifique du gaz idéal. On considère également les données p - V - T (pression-volume-température) de la phase unique. Les données sur la saturation et le gaz idéal sont représentées sous forme de simples corrélations. Les fluides susceptibles de remplacer les chlorofluorocarbures entièrement halogénés sont les suivants: R23, R32, R125, R143a, R22, R134a, R152a, R124, R142b et R123.

(Mots clés: propriété thermodynamique; substitut des CFCs)

In order to evaluate the performance of possible alternatives to the fully halogenated chlorofluorocarbons (CFCs) as working fluids in refrigeration or heat pumping applications, knowledge of the thermophysical properties is required. The thermodynamic (or equilibrium) properties of the refrigerant largely determine the energy efficiency and capacity of the vapour compression cycle and are thus the key data needed in designing equipment and in comparing one working fluid with another. The transport properties have a major impact on equipment design (particularly of heat exchangers) and thus influence whether it is economically feasible to build a machine which can actually obtain the theoretical efficiency of the thermodynamic cycle.

The evaluation of a number of promising new refrigerants has been hampered by the lack of property data. This paper begins to address this problem by compiling, evaluating and correlating key thermodynamic data for selected fluids. Considered are the critical and triple point parameters, vapour pressure, saturated liquid density, ideal gas heat capacity and the single-phase pressure-volume-temperature (p - V - T) properties. This paper is the first instalment of what is expected to be a continuing activity; it is not all-inclusive and, indeed, the author would appreciate information on data sources that are

not included. Other important properties, such as surface tension and the transport properties of viscosity and thermal conductivity, will be considered in the future.

The fluids considered include the leading candidates to replace the fully halogenated CFCs: R23, R32, R125, R143a, R22, R134a, R152a, R124, R142b and R123. These fluids are all hydrogen-containing halogenated methanes and ethanes. The range of normal boiling points for these candidate fluids is similar to that seen with the fully halogenated compounds. While other fluids, such as R134, R123a and R141b, and other classes of fluids, such as fluorinated propanes and ethers, show promise as refrigerants, there is insufficient data on these other compounds to warrant inclusion in the present work.

In many instances, the fluids considered here have never been commercially produced and, as a consequence, the data for many of them are sparse; thus, all possible sources of data have been utilized. These include the published literature (as revealed by a search of *Chemical Abstracts* and surveys such as that by Stewart *et al.*¹), compilations such as that by the Japanese Association of Refrigeration², prepublication versions of manuscripts received from several groups, and, finally, unpublished data provided by several chemical manufacturers. Where available, preference is generally given to published over unpublished sources. The data differ greatly in quality and reliability and, as will be seen, are sometimes conflicting.

To be of maximum and immediate use, all data are fitted with standard forms and presented primarily in

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Table 1 Fluid fixed points (SI Units)
Tableau 1 Caractéristiques des fluides (Système SI)

Fluid	Chemical formula	Molecular mass (g mol ⁻¹)	Triple point (K)	Normal boiling point		Critical point		
				Temperature (K)	Liquid density (kg m ⁻³)	Temperature (K)	Pressure (kPa)	Density (kg m ⁻³)
R23	CHF ₃	70.013	117.97	191.1	1457	298.98	4820	526
R32	CH ₂ F ₂	52.024	137	221.4	1215	351.56	5830	430
R125	CF ₃ CHF ₂	120.020	170	224.6	1515	339.4	3631	572
R143a	CH ₃ CF ₃	84.040	161.82	225.8	1176	346.25	3811	434
R22	CHClF ₂	86.468	113	232.3	1410	369.30	4988	513
R134a	CF ₃ CH ₂ F	102.030	172	247.0	1375	374.21	4056	515
R152a	CHF ₂ CH ₃	66.050	156	249.0	1011	386.44	4520	368
R124	CHClFCF ₃	136.475	74	261.1	1472	395.65	3634	560
R142b	CH ₃ CClF ₂	100.495	142	263.9	1193	410.25	4246	435
R123	CHCl ₂ CF ₃	152.930	166	301.0	1456	456.94	3674	550

Table 2 Fluid fixed points (I-P Units)
Tableau 2 Caractéristiques des fluides (Unités I-P)

Fluid	Chemical formula	Molecular mass (lb lb ⁻¹ mol ⁻¹)	Triple point (°F)	Normal boiling point		Critical point		
				Temperature (°F)	Liquid density (lb ft ⁻³)	Temperature (°R)	Pressure (psia)	Density (lb ft ⁻³)
R23	CHF ₃	70.013	-247.3	-115.8	90.94	538.16	78.49	32.84
R32	CH ₂ F ₂	52.024	-213	-61.1	75.84	632.81	173.14	26.84
R125	CF ₃ CHF ₂	120.020	-154	-55.3	94.57	610.9	151.25	35.71
R143a	CH ₃ CF ₃	84.040	-168.4	-53.2	73.40	623.25	163.58	27.09
R22	CHClF ₂	86.468	-256	-41.4	88.01	664.74	205.07	32.03
R134a	CF ₃ CH ₂ F	102.030	-150	-15.1	85.84	673.58	213.91	32.15
R152a	CHF ₂ CH ₃	66.050	-179	-11.4	63.14	695.59	235.92	22.97
R124	CHClFCF ₃	136.475	-326	10.3	91.90	712.17	252.50	34.96
R142b	CH ₃ CClF ₂	100.495	-204	15.3	74.45	738.45	278.78	27.16
R123	CHCl ₂ CF ₃	152.930	-161	82.1	90.89	822.49	362.82	34.34

Note: None of the critical densities are known to four significant figures; they are given to this level for consistency with Table 2

terms of the resulting correlations. The forms of these correlations were chosen primarily for convenience and expediency; while theoretically reasonable, they do not necessarily reflect the theoretical state of the art. These correlations also serve as a convenient means of comparing data from different sources. In this report a summary section containing coefficients to the correlations precedes a detailed discussion of the data themselves.

Summary

Fluid fixed points

The triple point, normal boiling point and critical point parameters are fundamental characteristics of a fluid. The triple point is the state at which three phases (solid, liquid and vapour) coexist; it is virtually identical with the more often reported freezing point. The normal boiling point is simply the temperature at which the vapour pressure of a fluid is one standard atmosphere (101.325 kPa, 14.696 psia). As the vapour pressures of nearly all fluids are approximately parallel when plotted as the logarithm of pressure versus inverse temperature, the normal boiling point is a rough predictor of the vapour pressure at all temperatures. The critical point is the state at which the properties of the saturated liquid and vapour become indistinguishable: coexisting liquid and vapour are possible only at temperatures and pressures below the critical point values.

These parameters, often in the absence of any other information, are frequently used in screening many

different compounds to select a more limited set for further study. For many applications they define the temperature limits for the use of a particular fluid. Clearly a refrigerant cannot be used below the triple point temperature. For many refrigeration applications, operation at sub-atmospheric pressures is avoided and, thus, the normal boiling point is a more practical lower limit. Vapour compression refrigeration equipment transports heat through condensation and evaporation (i.e. two-phase) processes and thus the critical point represents an upper temperature and pressure limit. The critical point parameters are the essential inputs to estimation techniques based on the law of corresponding states, which is the observation that, when scaled by the critical parameters, the properties of nearly all fluids are similar.

The triple point, normal boiling point and critical point parameters of the refrigerants in question are given in Tables 1 and 2. The normal boiling point listed in this table is obtained by finding the temperature at which the vapour pressure correlation [Equation (1) discussed below] yields a pressure of one standard atmosphere. In Tables 1 and 2, and all subsequent tables, the fluids are listed in order of increasing normal boiling point temperature. All temperatures in this work are according to the IPTS-68 scale. The selection of these values is discussed in detail later in this paper.

Vapour pressure

The experimental vapour pressure data were fitted to the following equation, which is a modification of a form

Table 3 Vapour pressure
Tableau 3 Pression de vapeur

Fluid	Lower temperature limit		Coefficients to Equation (1)				RMS error (%)
	(K)	(°F)	a_1	a_2 (dimensionless)	a_3	a_4	
R23	134	-218	-9.682616	2.550689	4.104477	1.882155	0.43
R32	149	-191	-10.052244	2.844032	4.108620	3.450397	0.29
R125	233	-40	-11.674144	4.524166	4.567844	6.904302	0.10
R143a	185	-127	-7.451908	0.196624	3.658045	-5.178402	0.29
R22	203	-94	-8.985153	2.125014	3.693854	0.906855	0.09
R134a	210	-82	-8.798572	1.379055	3.587903	-2.390161	0.16
R152a	273	32	-4.133708	-3.135972	0.945576	-11.934945	0.11
R124	222	-60	-10.034418	2.870485	4.232259	1.619401	0.16
R142b	212	-78	-10.178263	2.964608	4.852732	3.542389	0.48
R123	273	32	-7.600976	0.365524	3.214724	-4.998549	0.09

Note: Upper temperature limit of correlation is the critical temperature except for R142b (369 K or 205°F)

Table 4 Saturated liquid density
Tableau 4 Densité de liquide saturé

Fluid	Lower temperature limit		Coefficients to Equation (2)				RMS error (%)
	(K)	(°F)	d_1	d_2	d_3 (dimensionless)	d_4	
R23	206	-89	2.568471	-1.636763	2.945022	-0.983341	0.19
R32	248	-13	1.667251	2.720934	-4.374005	3.272961	0.24
R125	229	-47	1.959463	0.847479	-0.840846	0.797769	0.02
R143a	197	-105	2.284033	-0.304060	2.235519	-1.995317	0.14
R22	213	-76	2.191954	0.046237	0.207547	0.397319	0.05
R134a	200	-100	1.986361	0.677576	-0.455932	0.592428	0.13
R152a	223	-58	2.456208	-1.665948	3.933187	-2.045507	0.18
R124	215	-73	2.064566	0.387932	-0.405756	0.715925	0.20
R142b	194	-110	-0.216863	9.627387	-12.788355	6.355207	0.31
R123	210	-82	2.119619	0.076919	0.313401	0.232851	0.20

Note: Upper temperature limit of correlation is the critical temperature except for R124 (390 K or 242°F) and R142b (369 K or 205°F)

suggested by Friend *et al.*³:

$$\ln(p/p_c) = a_1\tau/(1-\tau) + a_2\tau + a_3\tau^{1.89} + a_4\tau^3 \quad (1)$$

where p is pressure, p_c is the critical pressure and $\tau = (1 - T/T_c)$, with T and T_c in absolute temperature units (Kelvins or degrees Rankine). The term with the exponent of 1.89 arises from theories for asymptotic critical behaviour. Friend *et al.*³ include an additional empirical term proportional to τ^2 ; this term was deleted here because the data for refrigerants generally does not justify two terms which are statistically so very similar.

The coefficients for each of the fluids considered, along with the temperature range of the correlation, are given in Table 3. Modest extrapolations outside this range should yield fairly accurate results. This table also gives the RMS deviations between Equation (1) and the input data. These RMS values serve as rough indicators of the precision of the data and the agreement between different sources. Particularly for those fluids with only one data source, the method of computing RMS deviations cannot detect any systematic errors in the data, and thus RMS values provide little information on the accuracy of the data and the resulting correlation. This is considered in more detail in the Discussion section.

Saturated liquid density

Liquid densities along the saturation line, ρ , were fitted to

the commonly used form:

$$\rho/\rho_c = 1 + d_1\tau^\beta + d_2\tau^{2/3} + d_3\tau + d_4\tau^{4/3} \quad (2)$$

where $\tau = (1 - T/T_c)$ and ρ_c is the critical density. The term with the exponent β gives the correct behaviour near the critical point; an 'effective' value of $\beta = 0.355$ is used here. The higher order terms are empirical. Equation (2) has the proper form over a wide range of temperature including the vicinity of the critical point, and it, or slight variations on it, are often used in the correlation of saturated liquid densities. The fit of density data to Equation (2) is summarized in Table 4. As with vapour pressure, the applicable temperature range of the correlation and the RMS deviation are also given. The critical temperature and density required in Equation (2) may be found in Tables 1 and 2.

Ideal gas heat capacity

The isobaric heat capacity of the ideal gas state, C_p° , (vapour in the limit of zero pressure) is required to fully define the thermodynamic behaviour of a fluid. Specifically, the ideal gas heat capacity as a function of temperature is needed to calculate the temperature dependence of enthalpy and entropy from a pressure-volume-temperature equation of state.

These heat capacities can be directly determined by calorimetric measurements. This is a very difficult measurement because of the very dilute nature of the

Table 5 Ideal gas heat capacity
Tableau 5 Capacité thermique du gaz idéal

Fluid	Coefficients to Equation (3)				RMS error (%)
	c_0	c_1	c_2 (dimensionless)	c_3	
R23	3.390384	0.886176	2.839103	-0.967486	0.08
R32	4.424901	-2.661170	5.580232	-1.680558	0.05
R125	2.838680	11.581633	-1.704482	-0.266732	0.03
R143a	2.154036	8.979986	-0.021508	-0.678740	0.05
R22	2.241433	6.408781	-0.510996	-0.403409	0.04
R134a	2.018320	12.888065	-3.828818	0.714145	0.04
R152a	3.421564	3.937963	4.399060	-1.969414	0.04
R124	3.941838	10.417617	1.082720	-1.370683	0.42
R142b	2.054977	13.016838	-2.771827	-0.155394	0.25
R123	0.724188	27.762732	-19.165589	5.947808	0.16

Note: Temperature limits of correlation for all fluids are 150–500 K (–190 to 440°F); the gas constant, $R=8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ (1.986 BTU lb⁻¹ mol⁻¹ R⁻¹)

sample and, consequently, such measurements are not common. Ideal gas heat capacities are most often computed from spectroscopic data using the methods of statistical mechanics. These computations can yield excellent values for C_p° but become hopelessly complex as the number of atoms in a molecule increases. The practical limit for this method is a substituted ethane (most of the refrigerants considered here are substituted ethanes). Finally, ideal gas heat capacities can be derived from measurements of the speed of sound in the low pressure vapour. This is perhaps the most reliable method for molecules with two or more carbon atoms.

Heat capacities for the ideal gas state are correlated in terms of a simple polynomial:

$$C_p^\circ/R = c_0 + c_1 T_r + c_2 T_r^2 + c_3 T_r^3 \quad (3)$$

where $T_r = T/T_c$ and R is the gas constant ($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$, $1.986 \text{ BTU lb}^{-1} \text{ mol}^{-1} \text{ R}^{-1}$). The coefficients for Equation (3) are given in Table 5. As with the saturation data, the details of the data sources for each fluid are given in the Discussion section.

p–*V*–*T* properties

The single-phase, *p*–*V*–*T* behaviour of a fluid is, along with the saturation data, the key information needed to fit an equation of state. An equation of state is a function that can correlate the thermodynamic properties of a fluid in a consistent way. Further, it, in conjunction with a formulation for the ideal gas heat capacity, comprises a fundamental relationship from which all the thermodynamic properties of a fluid can be derived by applying the appropriate thermodynamic operations. An equation of state thus allows the calculation of quantities, such as entropy, that may not have been, or cannot be, directly measured. The *p*–*V*–*T* data available for each fluid are graphically depicted in the Discussion section.

Discussion

R23

Several extensive data sets exist for R23 (trifluoromethane). Valentine *et al.*⁴ have measured the triple point temperature. As summarized by Hori *et al.*⁵, at least nine groups have measured one or more of the critical

parameters. While some of the earlier values differ widely, the values measured after 1958 are in essential agreement. The critical temperature and density of Shavandrin⁶ (as reported by Hori *et al.*⁵) are adopted here because of the high stated accuracy and high purity (99.99%) sample used. There has apparently not been an accurate direct determination of the critical pressure and, thus, the value reported in Tables 1 and 2 is an extrapolation of the vapour pressure data.

Vapour pressures for R23 have been reported from a few degrees above the triple point to within a fraction of a degree of the critical temperature. Four data sets have been used in fitting the parameters to Equation (1). The residuals are shown in Figure 1(a). The widest ranging data are those of Hou and Martin⁷. The data of Hori *et al.*⁵ are high compared to those of Hou and Martin⁷; they are given zero weight in the fit, primarily because of the relatively impure (99.1%) sample used. [In Figure 1(a) and all similar figures, points used in the correlation are shown as filled-in symbols; points excluded from the fit are shown as open symbols.] Below the normal boiling point, differences of as much as 1.5% exist between the three data sets (Hou and Martin⁷, Popowicz *et al.*⁸, Valentine *et al.*⁴). The study of Popowicz *et al.*⁸ examined the effect on vapour pressure of R23 with differing isotopic concentrations; the data used here are those for ¹²CHF₃.

The correlation of saturated liquid densities is based on the data of Löffler⁹, as reported by Döring and Löffler¹⁰. The eight data points of Hou and Martin⁷ are consistently below the Löffler data [as indicated in Figure 1(b)] and were not used in fitting Equation (2).

Ideal gas heat capacities have been calculated from spectroscopic data by at least three groups. The calculations of Valentine *et al.*⁴ are in excellent agreement with those in the JANAF Tables¹¹. The values of Rodgers *et al.*¹² are a few tenths of a percentage higher.

The *p*–*V*–*T* data for R23 are the most extensive and wide ranging of any of the fluids considered in this report. The measured points are shown in Figure 1(c). (In this figure, and all similar figures, points plotted just outside the frame of the plot are out of range and are not to scale.) Rubio *et al.*¹³ have measured over 1300 points along 24 isotherms from just above the triple point temperature to 332 K (138°F) at pressures up to 10 MPa (15 900 psia). The reported accuracy of these points is very good [uncertainties of 0.02 K (0.04°F) in temperature, 0.1% or

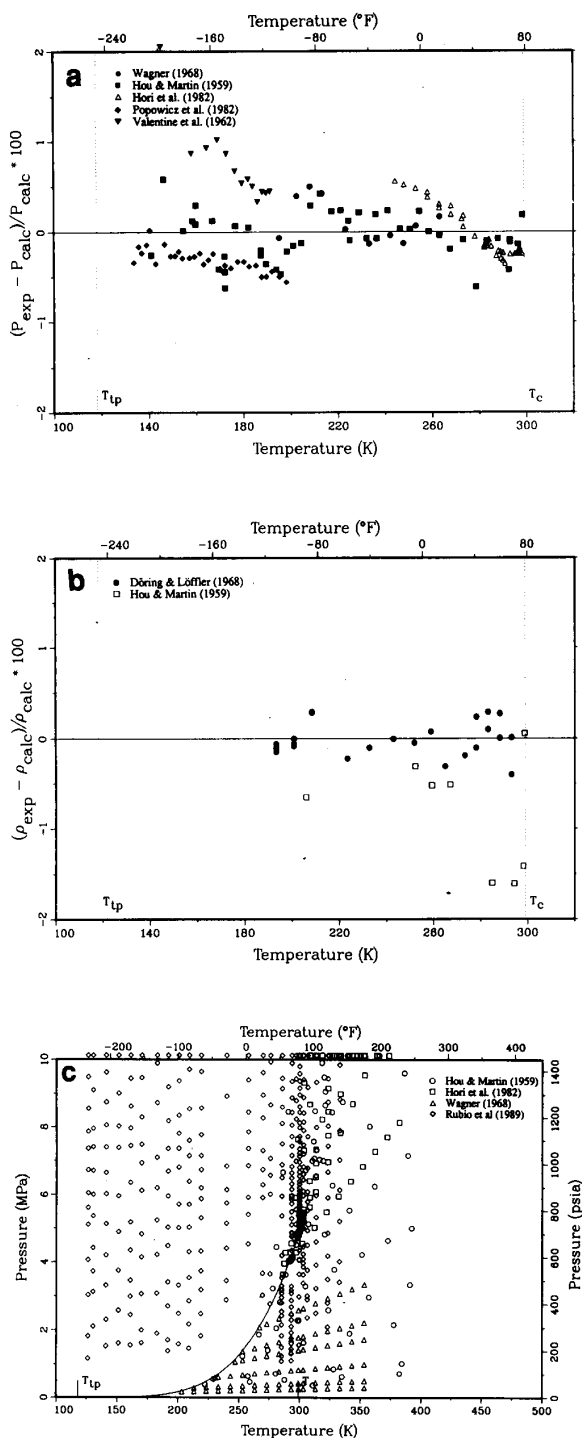


Figure 1 R23 (a) Comparison of vapour pressure correlation with data (filled and open symbols indicate points used and not used, respectively, in fitting correlation); (b) comparison of saturated liquid density correlation with data; and (c) available p - V - T data (line indicates saturation boundary)

Figure 1 R23 (a) Comparaison de la corrélation de la pression de vapeur avec des données (les symboles pleins et vides indiquent respectivement les points utilisés et non utilisés pour l'élaboration de corrélations); (b) comparaison de la corrélation de densité de liquide saturé avec des données; et (c) données pression-volume-température disponibles (la ligne indique la limite de saturation)

better in pressure and 0.1–0.4% in density] with a sample purity of better than 99.9%. Additional data have been measured by Hou and Martin⁷, Wagner¹⁴ and Hori *et al.*⁵.

R32

The primary source for the properties of R32 (difluoromethane) was the work of Malbrunot *et al.*¹⁵. They conducted a comprehensive set of measurements, including a critical point determination. The triple point temperature is from Johns¹⁶.

For vapour pressures, there is one source in addition to Malbrunot *et al.*¹⁵. Kanungo *et al.*¹⁷ have measured the vapour pressures of R32 with various isotopic compositions to a very high precision (better than 0.01%). They do not present their data but do give a correlation which represents their 138 measurements of 'the vapour pressure of the natural abundance of methylene difluoride at temperatures between 149 and 245 K'. This correlation was used to calculate vapour pressures over a similar range of temperature which were used in fitting the parameters to Equation (1). Although the scatter for the data of Malbrunot *et al.*¹⁵ is fairly large, there is good agreement between the two sources, as shown in Figure 2(a).

The saturated liquid densities of Malbrunot *et al.*¹⁵ were used to fit the parameters of Equation (2). The residuals are given in Figure 2(b).

Heat capacities in the ideal gas state have been computed from spectroscopic data by Rodgers *et al.*¹² and JANAF¹¹. The values computed by these two sources are virtually identical, which should not be surprising given the simplicity of the molecule and the common set of spectroscopic data used.

The p - V - T properties of R32 have been measured by Malbrunot *et al.*¹⁵ along 16 isotherms from 248 to 473 K (–13 to 392 °F) at pressures up to 20 MPa (2900 psia). The measured data are shown in Figure 2(c).

R125

The data for R125 (pentafluoroethane) are limited. The critical temperature adopted here was reported by Shankland *et al.*¹⁸. The triple point temperature and critical density used here were reported on a manufacturer's data sheet¹⁹. The critical pressure given in Tables 1 and 2 was calculated by an extrapolation of the vapour pressure data to the critical temperature.

The only source for saturation data is Shankland *et al.*¹⁸. A comparison of these data with the correlation is presented in Figure 3(a).

The eight liquid densities of Shankland *et al.*¹⁸ over the temperature range 228.7–336.3 K (–48.0 to 145.7 °F) were measured using glass flotation beads of known density. In this technique, the temperature of the fluid is adjusted so that the density of the fluid matches that of one of the beads. In another work by the same group²⁰, the accuracy of this method is stated to be 0.2 kg m^{-3} (0.01 lb ft^{-3}).

Ideal gas heat capacities are calculated by Chen *et al.*²¹ based on spectroscopic data. No p - V - T data for R125 could be found.

R143a

Only limited measurements on the properties of R143a (1,1,1-trifluoroethane) have been reported, with most of the information from just two sources. Russell *et al.*²²

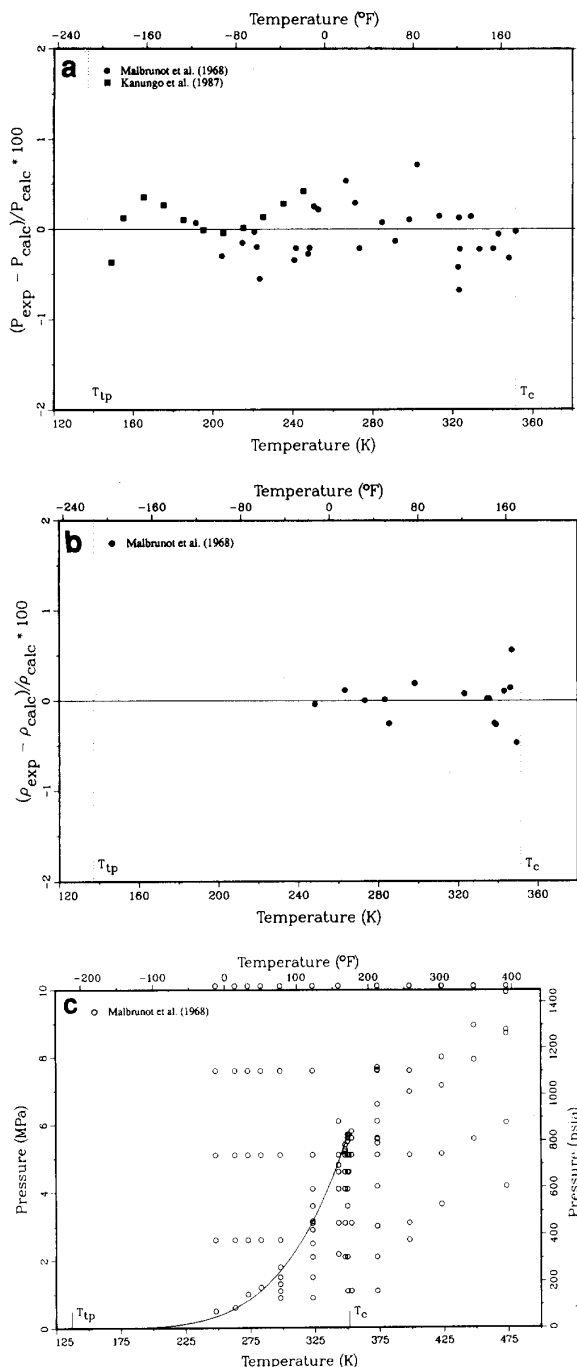


Figure 2 R32 (a) Comparison of vapour pressure correlation with data; (b) comparison of saturated liquid density correlation with data; and (c) available p - V - T data

Figure 2 R32 (a) Comparaison de la corrélation de la pression de vapeur avec des données; (b) comparaison de la corrélation de densité de liquide saturé avec des données; et (c) données pression-volume-température disponibles

measured the triple point temperature with an uncertainty of 0.04 K (0.07°F). Mears *et al.*²³ measured the critical temperature with an uncertainty of 0.5 K (0.9°F); their reported critical density, which is also used here, was computed from the rectilinear diameter.

The critical pressure used here is an extrapolation of the vapour pressure data of Mears *et al.*²³ to their critical temperature.

Vapour pressure and saturated liquid density data are reported by Russel *et al.*²² below the boiling point temperature and by Mears *et al.*²³ at higher temperatures; there is little or no overlap between the two data sets. The vapour pressure data of Russell *et al.*²² are of good precision. The systematic deviation between these data and Equation (1) seen in Figure 4(a) may be the result of inconsistencies between the two data sources.

Mears *et al.*²³ estimate their liquid densities to be accurate to 0.2% and these data were given a higher weight than those of Russel *et al.*²² in fitting Equation (2). The residuals for this fit are shown in Figure 4(b).

The fit of ideal gas heat capacities to Equation (3) is based on the values reported by Chen *et al.*²¹. They evaluated more than 20 literature sources of electron diffraction measurements, structural data, and microwave, Raman and infrared spectra. They found often conflicting assignments for the fundamental vibrational frequencies reported in the literature. Their calculated ideal gas heat capacities are based largely on the vibrational assignments of Smith *et al.*²⁴. Thus it is not

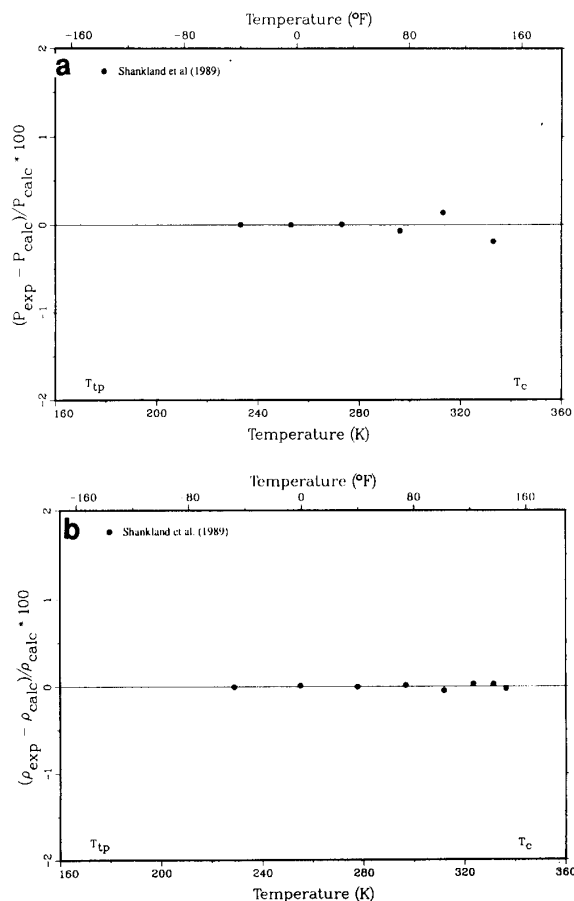


Figure 3 R125 (a) Comparison of vapour pressure correlation with data; and (b) comparison of saturated liquid density correlation with data

Figure 3 R125 (a) Comparaison de la corrélation de la pression de vapeur avec des données; et (b) comparaison de la corrélation de densité de liquide saturé avec des données

surprising that the values of Chen *et al.*²¹ are similar to the values calculated by Smith *et al.*²⁴. The single calorimetric value of Vanderkooi and De Vries²⁵ is 10.6% below that predicted by Equation (3) and was given zero weight in the correlation.

The only source of p - V - T data is Mears *et al.*²³. Their

21 data points were measured along five isochores as shown in Figure 4(c).

R22

The extensive body of data on R22 (chlorodifluoromethane) is summarized, evaluated and correlated in the treatise by the Japanese Association of Refrigeration (JAR)². The data sources recommended by the JAR were largely adopted here so that the limited time available for this project could be better expended on other fluids for which no such compilations exist. In addition, several works published since 1975 have also been included.

The triple point temperature has been measured by Neilson and White²⁶. ASHRAE²⁷ reports a value which is 2.7 K (4.9°F) lower but does not fully document the source, and thus the experimental value of Neilson and White²⁶ is adopted here. Both the JAR² and Kohlen *et al.*²⁸ have examined the available critical point data and recommend identical values for the critical parameters; their recommendations are adopted here.

The vapour pressure data of Kletskii, Kohlen^{28,29} and Zander³⁰ were fitted in Equation (1); the residuals are shown in Figure 5(a). Zander's point at 366.1 K (199.3°F) was excluded from the fit because it appeared to be anomalously low compared to the other data sets. [In Figure 5(a) and all similar residual plots, points used in the correlation are shown as filled-in symbols; points excluded from the fit are shown as open symbols.]

The correlation for saturated liquid density [Equation (2)] was fitted to the data of Zander³⁰, Okada *et al.*³² and Kohlen *et al.*²⁸. All three data sets are in excellent agreement below about 350 K (170°F); above this temperature, the values of Okada *et al.*³² and Zander³⁰ diverge. The data of Zander³⁰ were more consistent with the selected critical density and were thus used for the fit at temperatures above 350 K (170°F).

For the ideal gas heat capacity, the values presented in the JANAF tables¹¹ are the basis for the fit to Equation (3). These are calculated from spectroscopic data and are based on a thorough survey of the literature. The JAR² reports that several other calculations of C_p^0 are in essential agreement with the JANAF values. The values of Rodgers³¹ are as much as 2.5% lower than those of JANAF. Such a large discrepancy is unusual for a single-carbon molecule. Ernst and Büsser³³ have directly measured the low pressure heat capacity of R22; their values for C_p^0 (obtained by extrapolation to zero pressure) are about 1.5% lower than the values adopted here.

Four sources of p - V - T data are indicated in Figure 5(c). The data of Michels (as reported by Martin³⁴) cover the range below about the critical density. The measurements of Kohlen²⁸ and Kumagi and Iwasaki³⁵ are in the liquid density region, with the later data set extending to very high pressures (160 MPa, 23 200 psia). The most wide-ranging data are those of Zander³⁰, who employed isochoric and Burnett techniques along lines of constant volume and temperature, respectively. Although extensive data are available in the vapour region, there is very little liquid data below 300 K (80°F) and none below 250 K (−10°F). If not for this deficit at low temperatures, R22 might be an excellent reference fluid for developing models for the entire class of polar refrigerants.

R134a

Refrigerant 134a (1,1,1,2-tetrafluoroethane) has been the

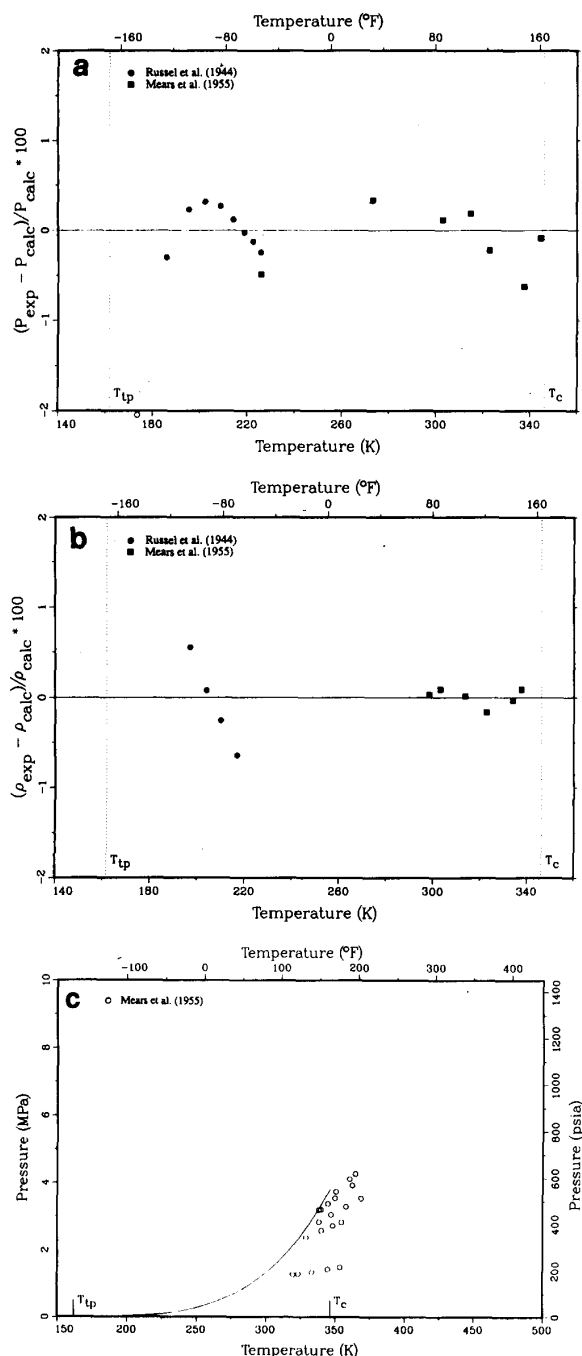


Figure 4 R143a (a) Comparison of vapour pressure correlation with data; (b) comparison of saturated liquid density correlation with data; and (c) available p - V - T data

Figure 4 R143a (a) Comparaison de la corrélation de la pression de vapeur avec des données; (b) comparaison de la corrélation de densité de liquide saturé avec des données; et (c) données pression-volume-température disponibles

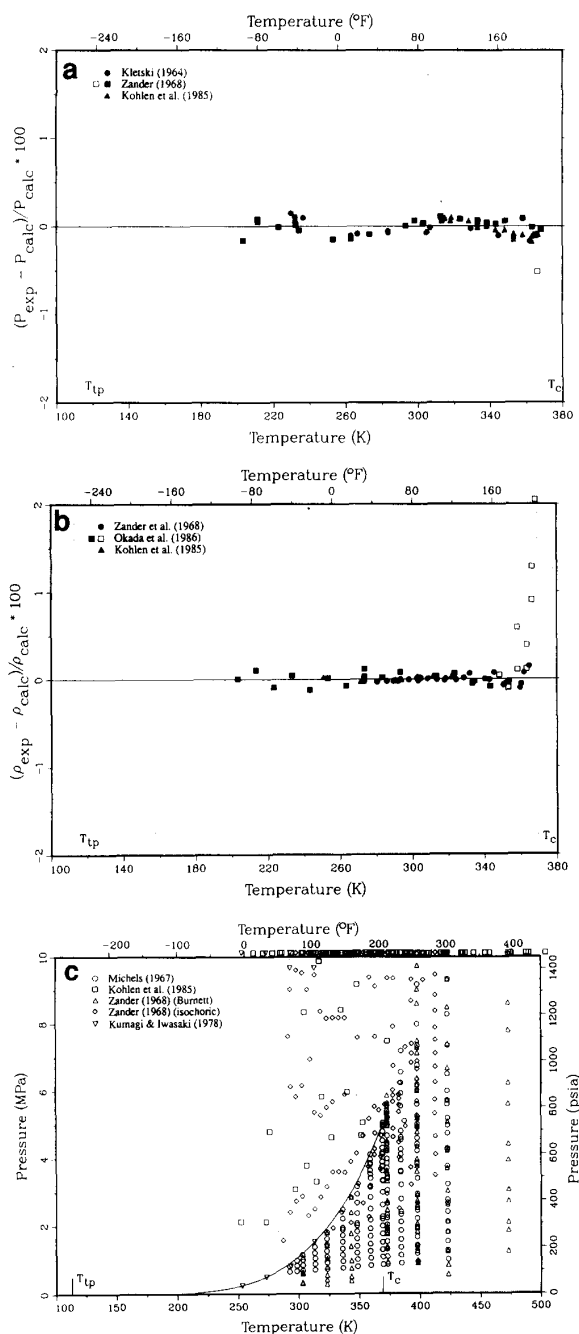


Figure 5 R22 (a) Comparison of vapour pressure correlation with data; (b) comparison of saturated liquid density correlation with data; and (c) available p - V - T data

Figure 5 R22 (a) Comparaison de la corrélation de la pression de vapeur avec des données; (b) comparaison de la corrélation de densité de liquide saturé avec des données; et (c) données pression-volume-température disponibles

focus of significant attention in the fluid property community recently, and considerable data have become available. Watanabe³⁶ has summarized the reported critical parameters. While the values documented in the literature are in very good agreement, the parameters reported on the data sheets of some of the chemical manufacturers often differ widely (spanning a range of

more than 6 K (10 °F) for the reported values of the critical temperature, for example). The determination of Morrison³⁷ is adopted here. Sukornick³⁸ reports a freezing temperature of 172 K (−150 °F).

Vapour pressures for R134a are reported by Wilson and Basu²⁰, Weber³⁹, Kubota *et al.*⁴⁰, Piao *et al.*⁴¹ and Maezawa *et al.*⁴². Together these data span a temperature range from 211.0 K (−79.7 °F) to within 1 K (2 °F) of the critical temperature. In addition, Yamashita *et al.*⁴³ have measured the vapour pressure of R134a at 25 temperatures from 253 to 371 K (−4 to 208 °F); their paper does not, however, give the experimental points. The data of Wilson and Basu²⁰, Weber³⁹ and Piao *et al.*⁴¹ are consistent and were used in fitting the coefficients to Equation (1). The data of Kubota *et al.*⁴⁰ and Maezawa *et al.*⁴² deviates from the other data sets [as indicated in Figure 6(a)], especially at high and low temperatures, respectively, and were not used in the fit.

Four sets of saturated liquid densities have been reported by two independent groups. Wilson and Basu²⁰ report nine measurements over a fairly wide range of temperature (238.9 to 371.6 K, −29.6 to 209.2 °F) using the floating bead technique. At Keio University, Kabata *et al.*⁴⁴ report six measurements in the vicinity of the critical point, Maezawa *et al.*⁴² have measured 25 densities from 200 to 370 K (−100 to 206 °F) and Piao *et al.*⁴¹ have determined seven points by extrapolation of their isochoric p - V - T data to the saturation line. Except for the near-critical data of Kabata *et al.*⁴⁴ and the point at 370 K (206 °F) of Maezawa *et al.*^{42,39} the data are in good agreement, as shown in Figure 6(b), and were used in fitting the coefficients to Equation (2).

The expression for ideal gas heat capacity [Equation (3)] is based on the values derived by Goodwin and Moldover⁴⁵ from their sound speed measurements on the low pressure vapour. The values calculated by Chen *et al.*²¹ and Wilson and Basu²⁰ from spectroscopic data are 1.2–2.7% higher than the values adopted here.

Wilson and Basu²⁰, Weber³⁹ and Piao *et al.*⁴¹ have all measured p - V - T data along isochores, as indicated in Figure 6(c). Maezawa *et al.*⁴² have carried out limited measurements along isotherms.

R152a

For R152a (1,1-difluoroethane), the critical point parameters reported by Higashi *et al.*⁴⁶ are adopted here, although those reported by Mears *et al.*²³ are the basis of the critical parameters listed on many manufacturers' data sheets. The two critical point determinations are consistent. The determination by Higashi *et al.*⁴⁶ is, however, of much higher accuracy. The freezing point reported by ASHRAE²⁷ is used here.

Higashi *et al.*⁴⁶ report 44 vapour pressure measurements from 273.1 K (32 °F) to within 0.4 K (0.07 °F) of the critical temperature with a precision better than 0.17%. Less extensive data are reported by Yada *et al.*⁴⁷ and Sato and Uematsu⁴⁸. Additional data, of lower accuracy but covering a wider temperature range, are reported by Mears *et al.*²³. The first three data sets are in good agreement [as indicated in Figure 7(a)] and were used in fitting the parameters to Equation (1). The data of Mears *et al.*²³ exhibit considerable scatter and are significantly different from the other sources; they were excluded from the fit to Equation (1). [In Figure 7(a) and all similar plots, points drawn just outside the frame of the plot

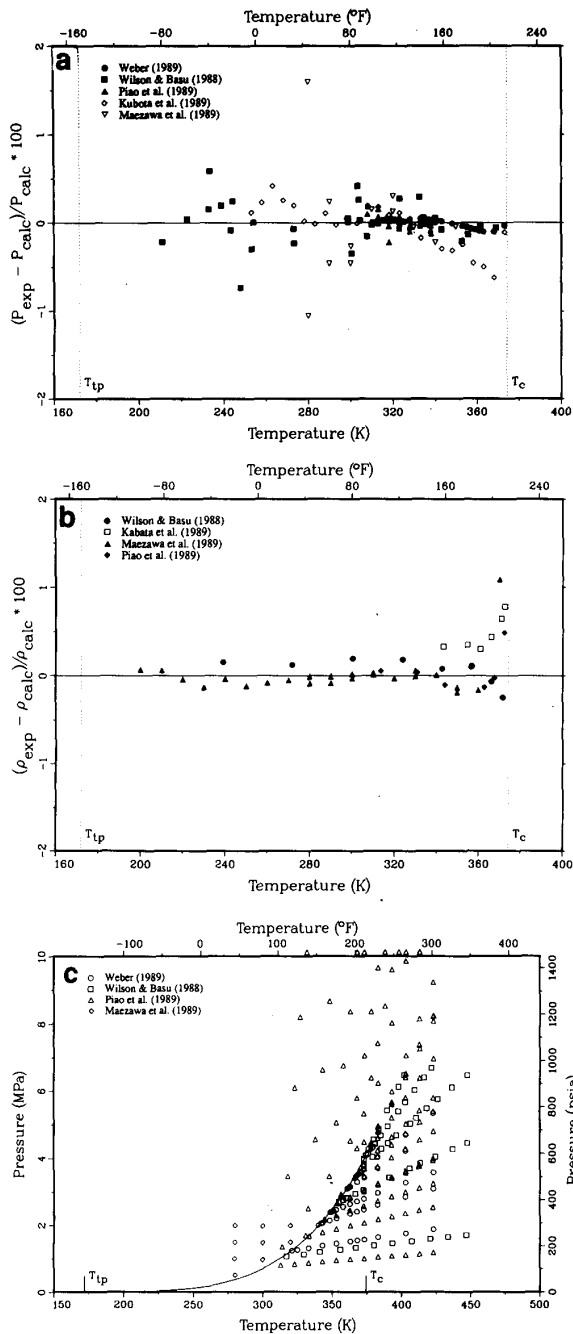


Figure 6 R134a (a) Comparison of vapour pressure correlation with data; (b) comparison of saturated liquid density correlation with data; and (c) available p - V - T data

Figure 6 R134a (a) Comparaison de la corrélation de la pression de vapeur avec des données; (b) comparaison de la corrélation de densité de liquide saturé avec des données; et (c) données pression-volume-température disponibles

indicate residuals greater than the limits of the ordinate and are not to scale.] All attempts to extend the range of Equation (1) to lower temperatures by including selected low temperature points of Mears *et al.*²³ resulted in a much poorer fit at the higher temperatures, suggesting inconsistencies among the different data sets.

Saturated liquid densities are reported by Sato *et al.*⁴⁸,

Higashi *et al.*⁴⁶, Masui *et al.*⁴⁹ and Mears *et al.*²³. The values reported by Sato *et al.*⁴⁸ were measured by Kanome and Fujita⁶⁹. All of these sources are in good agreement, as indicated in Figure 7(b), and all were used in the fit to Equation (2).

The ideal gas heat capacities are based on the calculated

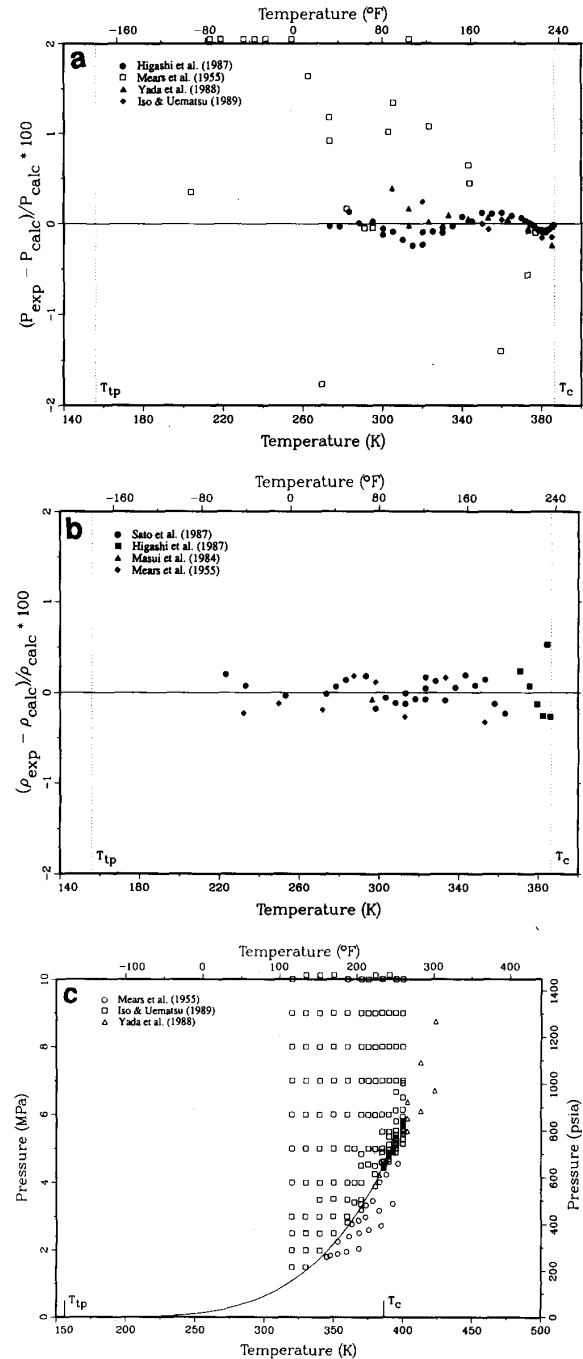


Figure 7 R152a (a) Comparison of vapour pressure correlation with data; (b) comparison of saturated liquid density correlation with data; and (c) available p - V - T data

Figure 7 R152a (a) Comparaison de la corrélation de la pression de vapeur avec des données; (b) comparaison de la corrélation de densité de liquide saturé avec des données; et (c) données pression-volume-température disponibles

values of Chen *et al.*²¹. These values are based on relatively limited spectroscopic data.

The p - V - T properties of R152a have been reported at low densities near the saturation line by Mears *et al.*²³, at near-critical densities by Yada *et al.*⁴⁷ and at moderately high densities by Iso and Uematsu⁵¹. Majima *et al.*⁵² have measured 55 p - V - T points in the vapour region by the Burnett method over the temperature range 340–390 K (152–242°F) and at pressures from roughly 200 kPa (29 psia) to near the vapour pressure; their paper does not, however, present the actual experimental data.

R124

Measurements of the thermodynamic properties of R124 (1-chloro-1,2,2,2-tetrafluoroethane) have been published by Kubota *et al.*⁵³. Their measurements include a critical point determination which is in good agreement with the parameters reported by Basu *et al.*⁵⁴. The critical temperature and density of Kubota *et al.*⁵³ are used here because of their higher stated accuracy. The critical pressure was obtained by extrapolating the vapour pressure data of Basu *et al.*⁵⁴ to the critical temperature. The only information on the triple point temperature was an undocumented value reported on a manufacturer's data sheet¹⁹. The value of 74 K (–326°F) seems anomalously low compared to the other ethane based refrigerants, but, if correct, would give R124 the greatest two-phase range of any fluid.

Although fairly comprehensive, the measurements of Kubota *et al.*⁵³ have two weaknesses. The first is a lower temperature limit of only 278 K (41°F). The second, more serious, problem is the fairly poor precision of the pressure measurements. An accuracy of 12 kPa (1.7 psia) is claimed for the vapour pressure measurements; this is equivalent to an error of 6% at the lowest temperature. The relative error would be smaller at higher temperatures and pressures, yet for temperatures between 300 and 350 K (80 and 170°F) there are serious discrepancies between the data of Kubota *et al.*⁵³ and the vapour pressure points reported by Basu *et al.*⁵⁴ [see Figure 8(a)]. Because of the wider temperature range of the Basu *et al.*⁵⁴ data and the good accuracy for other fluids measured by this group (e.g. Wilson and Basu²⁰), only this latter data set were used in fitting Equation (1). Further measurements on this fluid will be required to ascertain whether this was the proper choice.

For liquid density, the situation is considerably better. The available data sources are in good agreement, as shown in Figure 8(b). The saturated liquid densities reported by Kubota *et al.*⁵³ were obtained by extrapolating compressed liquid measurements to the saturation pressure. The stated accuracy of the density measurements is 0.09% with the extrapolation adding a perhaps comparable uncertainty. The point at 323.2 K (122.1°F) appeared to be an outlier and was excluded from the fit. Saturated liquid densities from 216 to 391 K (–71 to 244°F) were determined by Basu *et al.*⁵⁴ using their calibrated glass flotation beads.

Bender *et al.*⁵⁵ have experimentally measured the heat capacity of R124 at pressures from 100 to 1500 kPa (15 to 218 psia) with the ideal gas values obtained by extrapolation to zero pressure. The values reported by Rodgers³¹ are computed from apparently limited structural and spectroscopic data. These two sources agree at roughly 375 K (215°F) but diverge at higher temperatures. Although both sources were used in the fit of Equation (3),

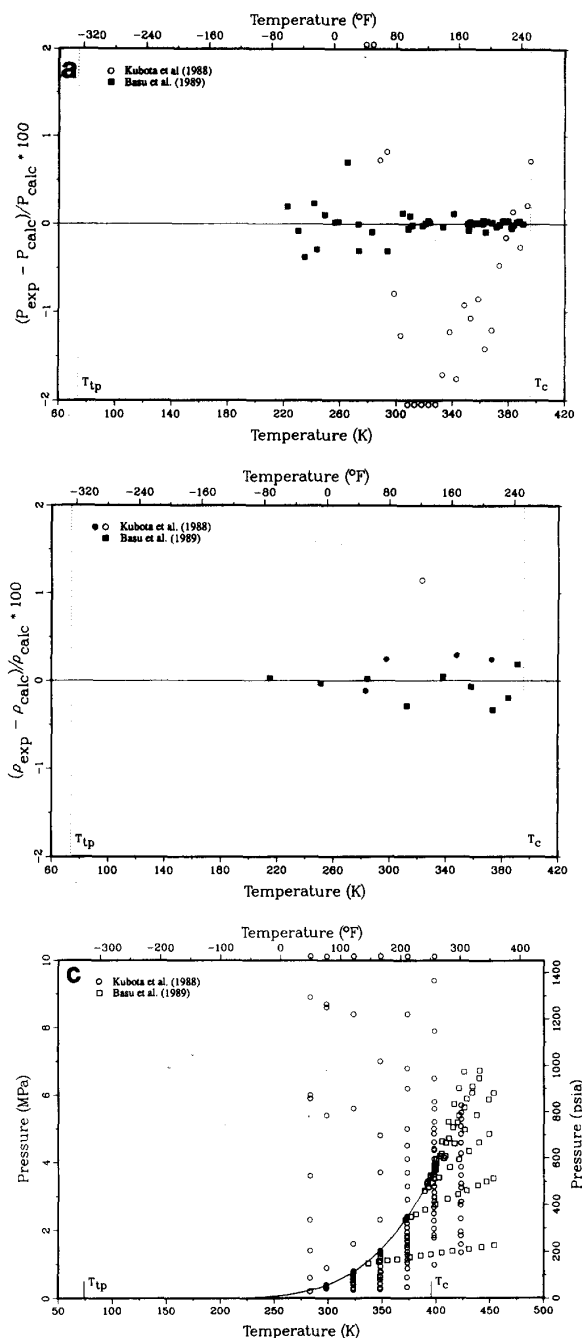


Figure 8 R124 (a) Comparison of vapour pressure correlation with data; (b) comparison of saturated liquid density correlation with data; and (c) available p - V - T data

Figure 8 R124 (a) Comparaison de la corrélation de la pression de vapeur avec des données; (b) comparaison de la corrélation de densité de liquide saturé avec des données; et (c) données pression-volume-température disponibles

the values of Rodgers³¹ were given a much lower weight than the data of Bender *et al.*⁵⁵.

Pressure-volume-temperature data for R124 have been reported by Kubota *et al.*⁵³ along seven isotherms extending from low pressure vapour to compressed liquid at up to 109 MPa (15 800 psia). Basu *et al.*⁵⁴ have

measured along seven isochores at the critical density and below. The measured points are indicated in Figure 8(c).

R142b

The long-standing reference for the thermodynamic properties of R142b (1-chloro-1,1-difluoroethane) has been Mears *et al.*²³; for example, the thermodynamic data of ASHRAE^{27,56} are taken directly from Mears *et al.*²³. Additional sources are Cherneeva⁵⁷ and Riedel⁵⁸. The critical temperature and density of Mears *et al.*²³ were selected for this work. The critical pressure was obtained by extrapolating the vapour pressure data of Cherneeva⁵⁷ to the critical temperature. The freezing temperature reported by ASHRAE²⁷ is adopted here.

The vapour pressure data of Riedel⁵⁵, Mears *et al.*²³ and Cherneeva⁵⁷ are fairly consistent, although there is considerable scatter, especially for the latter two sources, as shown in Figure 9(a). The data of Cherneeva⁵⁷ extended over a wider temperature range and gave a slightly better fit to Equation (1) and were thus selected over the data of Mears *et al.*²³. The data of Riedel⁵⁸ were also used in the correlation.

At temperatures above 320 K (116°F), the saturated liquid densities of Cherneeva⁵⁷ exhibit serious differences from the data of Mears *et al.*²³, Valtz *et al.*⁵⁹ and Riedel⁵⁸ [see Figure 9(b)]. These differences are at least an order of magnitude larger than can be explained by the accuracies of 0.1 and 0.2% claimed by Cherneeva⁵⁷ and Mears *et al.*²³, respectively. The data of Mears *et al.*²³, Valtz *et al.*⁵⁹ and Riedel⁵⁸ are fairly consistent and were used in fitting the coefficients to Equation (2). Maezawa *et al.*⁶⁰ have measured 36 saturated liquid densities over the temperature range 210–400 K (–82–260°F) but do not report their data.

The ideal gas heat capacities tabulated by Rodgers³¹ were used in fitting Equation (3). The values calculated by Smith²⁴ are 0.5 to 0.7% lower than those of Rodgers³¹.

Three sources of p – V – T data for R142b were found. None of these data sets are extensive and all are restricted to the low density vapour region. Proceeding from generally lower to higher densities they are: Riedel⁵⁸, Cherneeva⁵⁷ and Mears *et al.*²³. Kumagai *et al.*⁶¹ have measured 46 p – V – T points along 10 isochores with densities ranging from 71 to 970 kg m^{–3} (4.4 to 60.5 lb ft^{–3}) but do not report their data.

R123

Refrigerant 123 (1,1-dichloro-2,2,2-trifluoroethane) is, along with R134a, one of the two most publicized new refrigerants, and, thus, property data are starting to become available. An uncertainty involved with all R123 data is the isomeric purity of the sample. Commercial-grade R123 is likely to contain a significant percentage, perhaps as much as 10%, of the isomer R123a (1,2-dichloro-1,2,2-trifluoroethane). For some of the available data there is no information on whether the measurements were conducted on isomerically pure R123 or on the R123–R123a mixture produced by the process of a particular company.

Critical parameters have been measured by Weber and Levelt Sengers⁶², Tanikawa *et al.*⁶³ and Kamimura *et al.*⁵⁰ (as reported by Tanikawa *et al.*⁶³). These three determinations agree to within the stated experimental uncertainties. The measurements of Weber and Levelt Sengers⁶² were conducted on a high purity (99.99%)

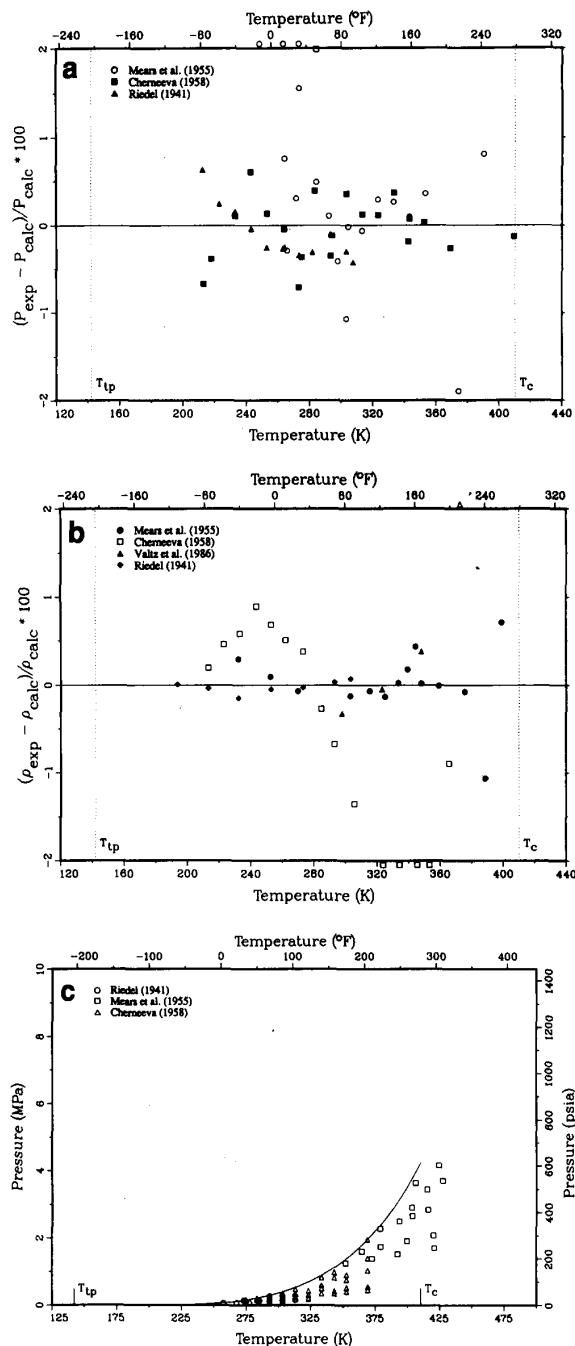


Figure 9 R142b (a) Comparison of vapour pressure correlation with data; (b) comparison of saturated liquid density correlation with data; and (c) available p – V – T data

Figure 9 R142b (a) Comparaison de la corrélation de la pression de vapeur avec des données; (b) comparaison de la corrélation de densité de liquide saturé avec des données; et (c) données pression–volume–température disponibles

sample with negligible R123a; for this reason, and others, their critical parameters are used here. The only triple point information that could be found was an undocumented freezing temperature reported by Sukornic³⁸.

Four sources for the vapour pressure of R123 are available. The data of Weber⁶⁴ and Yamashita *et al.*⁶⁵ are

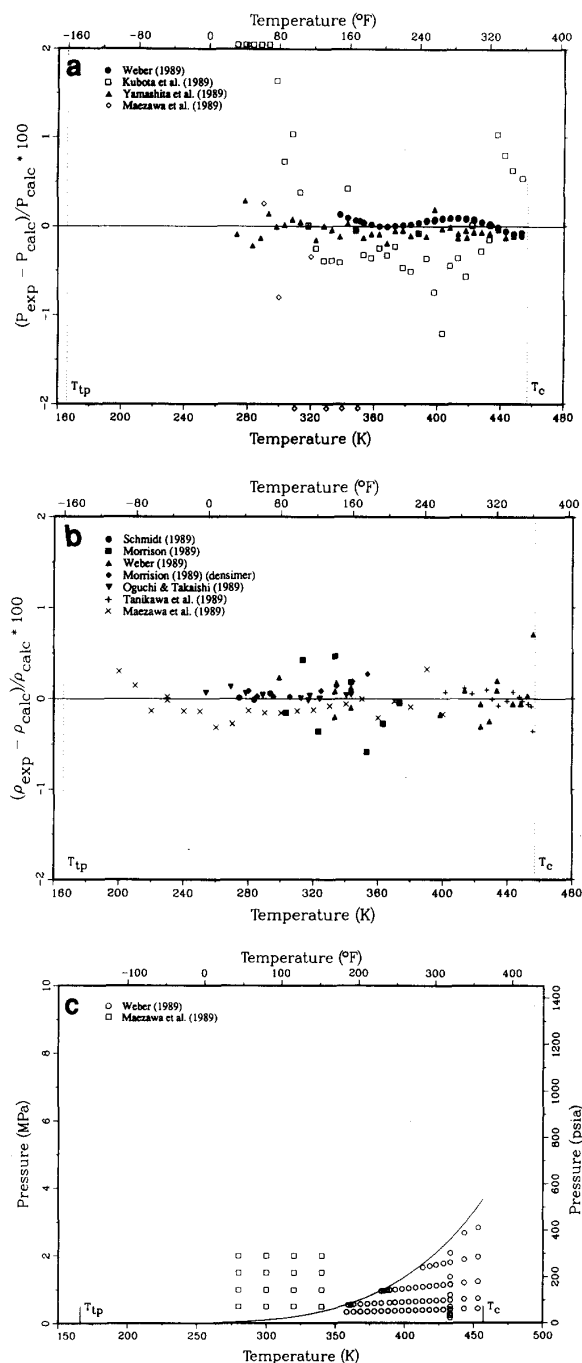


Figure 10 R123 (a) Comparison of vapour pressure correlation with data; (b) comparison of saturated liquid density correlation with data; and (c) available p - V - T data

Figure 10 R123 (a) Comparaison de la corrélation de la pression de vapeur avec des données; (b) comparaison de la corrélation de densité de liquide saturé avec des données; et (c) données pression-volume-température disponibles

in good agreement [see Figure 10(a)] and form the basis of the fit to Equation (1). The data of Kubota *et al.*⁴⁰ and Maezawa *et al.*⁴² exhibit considerable scatter and were not used in the fit.

No less than seven sets of data are available for the saturated liquid density of R123. At NIST, Schmidt⁶⁶ has

employed a buoyancy technique, Weber and Levelt Sengers⁶² have used a constant volume cell and Morrison⁵⁷ has used a mercury displacement variable-volume cell as well as a vibrating-tube densimeter. Oguchi and Takaishi⁶⁷ have used a glass float technique, Tanikawa *et al.*⁶³ used a gas expansion technique and Maezawa *et al.*⁴² employed a magnetic suspension densimeter. All of these data were felt to be of comparable accuracy and all were included in the fit of Equation (2). As indicated in Figure 10(b), the different data sets are in essential agreement, although exhibiting some scatter.

Ideal gas heat capacities were fitted to the values of Goodwin and Moldover⁴⁵ derived from sound speed measurements on low pressure vapour. The values of Luft⁶⁸ are in good agreement with those of Goodwin and Moldover⁴⁵; his points at 400 and 500 K (260 and 440°F) were also used in the fit of Equation (3) in order to extend its temperature range.

Only limited p - V - T data have been reported thus far for R123 [see Figure 10(c)]. Weber⁶⁴ has measured a total of 64 points along four vapour isochors and 11 points along an isotherm. Maezawa *et al.*⁴² have measured 16 points along four isotherms in the compressed liquid region.

Concluding remarks

This paper presents key thermodynamic properties of several alternatives to the fully halogenated chlorofluorocarbons. The quality of the data used in this compilation varies widely, ranging from well documented, high accuracy measurements from published sources to completely undocumented values listed on anonymous data sheets. That some properties for some fluids are available only from the latter type of source is clearly not the desired state of affairs. While some would reject all such data, the compilation given here is presented in the spirit of laying out the present state of knowledge and making available a set of data in a timely manner, even though its quality is sometimes uncertain. The correlations presented here are certain to change quickly as additional information becomes available. Indeed, one use of this paper could be to identify areas where additional work is needed.

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