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Correlations

Short Fundamental Equations of State for 20 Industrial Fluids

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In a preceding project, functional forms for "short" Helmholtz energy equations of state for typical nonpolar and weakly polar fluids and for typical polar fluids were developed using simultaneous optimization. In this work, the coefficients of these short forms for the equations of state have been fitted for the fluids acetone, carbon monoxide, carbonyl sulfide, decane, hydrogen sulfide, 2-methylbutane (isopentane), 2,2-dimethylpropane (neopentane), 2-methylpentane (isohexane), krypton, nitrous oxide, nonane, sulfur dioxide, toluene, xenon, hexafluoroethane (R-116), 1,1-dichloro-1-fluoroethane (R-141b), 1-chloro-1,1-difluoroethane (R-142b), octafluoropropane (R-218), 1,1,1,3,3-pentafluoropropane (R-245fa), and fluoromethane (R-41). The 12 coefficients of the equations of state were fitted to substance specific data sets. The results show that simultaneously optimized functional forms can be applied to other fluids out of the same class of fluids for which they were optimized without significant loss of accuracy. The high numerical stability of the functional forms resulted in successful fits for fluids that previously could not be described by accurate empirical equations of state. For R-41, it is shown that the accuracies can be increased further by fitting the temperature exponents in addition to the coefficients of the equation of state, provided that highly accurate experimental data are available. Typical uncertainties of properties calculated using the new equations are 0.2 % in density, 1 % to 2 % in heat capacity and liquid-phase speed of sound, and 0.2 % in vapor pressure. Where data are available, uncertainties in vapor-phase sound speeds are generally less than 0.1 %.

Introduction

The equations developed for calculating the thermodynamic properties of pure fluids have progressed over the years from simple cubic and virial equations of state to Beattie−Bridgeman and Benedict−Webb−Rubin (BWR) (1940) equations and then to the modified BWR (mBWR) equation and the fundamental equation of state explicit in the Helmholtz energy. Although the mBWR can be converted to the Helmholtz energy form, many equations developed in the Helmholtz energy form have advantages in terms of accuracy and simplicity. Most modern, high-accuracy equations of state for pure fluid properties are fundamental equations explicit in the Helmholtz energy as a function of density and temperature. All single-phase thermodynamic properties can be calculated as derivatives of the Helmholtz energy. The location of the saturation boundaries requires an iterative solution of the physical constraints on saturation (the so-called Maxwell criterion, i.e., equal pressures and Gibbs energies at constant temperature during phase changes), as is required with any form of the equation of state for thermodynamic consistency.

During the past 20 years or so, many of the industrial equations of state for fluids such as nitrogen, carbon dioxide, R-134a, and water have been replaced with high-accuracy fundamental equations of state developed from fitting state-of-the-art experimental measurements for density, phase equilibrium, heat capacity, and speed of sound. There are about 30 fluids that fit into this category, many of which have been outlined by Span et al. (2001) and Lemmon and Jacobsen (2005). Most of these fluids are fully characterized over the entire fluid surface by measurements, quite often with multiple publications for a single property over similar ranges of temperature and pressure. Jacobsen et al. (2000) and Span et al. (2001) reviewed the development and history of these equations.

The present work addresses the need for technical equations of state suited for advanced technical applications, such as process calculations including caloric properties, for these additional fluids where state-of-the-art measurements are not available and for which very low uncertainties are not required. Unlike highly accurate equations, which generally use 20 to 50 fluid-specific terms to describe densities to the order of (0.01 to 0.1) %, technical equations are shorter and often use fixed functional forms (a fixed functional form means that the number of terms and the temperature and density exponents are the same for all fluids, and only the coefficients are modified) to characterize the fluid properties. Examples include those of Bender (1970), Starling (1973), Polt (1987), and Platzer and Maurer (1989). More recently, Span and Wagner (2003a−c) developed two 12-term fundamental equations with fixed functional forms−one for nonpolar or slightly polar substances and one for polar fluids. Accurate data sets were used to develop the functional form and to assess the accuracy of the resulting equations of state. Thus, Span and Wagner concentrated on representing fluid properties for substances already described with high-accuracy equations of state. Although the new technical equations suffer from a slight loss in accuracy, their

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Table 1. Allowable Uncertainties in the Technical Equations of Span and Wagner (2003a−c)

	density	speed of sound	heat capacities	vapor pressure	saturated liquid density	saturated vapor density
$p \leq 30$ MPa	0.2 %	1 % to 2 %[a]	1 % to 2 %[a]	0.2 %	0.2 %	0.4 %
$p > 30$ MPa	0.5 %	2 %	2 %			

[a] 2 % at liquid states and at supercritical states with higher densities ($\rho > 0.5\ \rho_c$), 1 % at gaseous and gas-like supercritical states.

shorter forms allow for faster computations—from 2 to 10 times faster depending on the number of terms in other equations and on the use of special terms for increasing the accuracies in the critical region.

In this work, we build on the work of Span and Wagner (2003a−c) to substantially increase the number of fluids described by technical equations of state for industrial applications. For several fluids, the new equations presented here are the first attempt to depict the fluid's properties with multiparameter equations. For other fluids, the new equations replace older ones, many of which were presented by Polt (1987) with modified BWR functional forms or which used an extended corresponding states technique (Huber and Ely, 1994). The extended corresponding states technique is capable of characterizing the full fluid surface; however, it is computationally intensive and sometimes yields poor results in the vapor phase. Many of the older equations showed unphysical behavior such as calculated negative heat capacities at low temperatures. Some of the equations exhibit physically impossible behavior in accessible single-phase regions of the fluid surface. This unphysical behavior can be problematic in mixture models based on the pure fluid equations of state.

Polt (1987) published equations of state for carbon monoxide, hydrogen sulfide, krypton, sulfur dioxide, R-116, and R-142b. Polt et al. (1992) published equations for isopentane, neopentane, and toluene. Equations of state for krypton and sulfur dioxide are given in the publications of Polt and Maurer (1992) and Starling (1973). The equations of Polt (published in all three works) are based on the Bender equation of state (1970). This equation of state uses a pressure explicit extended virial equation with 20 terms modified from the BWR (Benedict et al., 1940) equation. Sakoda and Uematsu (2004) reported equations for hydrogen sulfide and isopentane. Juza and Sifner (1976) published an equation for krypton, and Sifner and Klomfar (1994) published an equation for xenon. These equations are piecewise Helmholtz energy equations of state and do not fit into the standard form commonly used today. An equation of state for R-41 is available in the open literature, although the source is difficult to obtain (Haynes, 1996) and the equation is valid only down to 175 K. Previous equations of state are available for carbon monoxide by Goodwin (1985) and for toluene by Goodwin (1989); however, these equations do not use the standard Helmholtz energy form and require special computer code to implement. Cibulka and Hnedkovsky (1996) reviewed the thermal properties of nonane and decane and reported Tait equations for both fluids, and Cibulka and Takagi (1999) reported similar information for toluene.

The technical equations of Span and Wagner (2003a−c) were developed with much foresight into the proper behavior of an equation of state. They extrapolate properly at low temperatures (as demonstrated by the curvature of the isobaric and isochoric heat capacities and the speed of sound) and at high temperatures (as demonstrated by the ideal curves). In addition, the number of terms in the equations (12 each) was kept to a minimum, thus decreasing the correlation among terms and the possibility of overfitting. Span and Wagner demonstrated the correlation among the 19 terms in Bender-type equations. Although the smaller number of terms decreases the flexibility of the equation and thus its ability to accurately represent a fluid's properties, its rigid shape becomes more applicable to substances with limited data and thus becomes a tool to fill in gaps in the thermodynamic surface, a key feature in modeling some of the fluids presented in this work.

The objective of Span and Wagner in the development of technical equations was the development of the best functional form (or forms) that considered the data for all substances fitted simultaneously, not the determination of a functional form that best fits the data. Thus, two forms were developed with the expectation that coefficients could be fitted for most fluids using either the nonpolar or the polar equation. In their work, the nonpolar form was used to describe the properties of the normal alkanes from methane to octane as well as the fluids argon, oxygen, nitrogen, isobutane, cyclohexane, and sulfur hexafluoride. Ethylene was included to ensure that the nonpolar form was capable of representing weakly polar fluids as well. The data sets for nitrogen and pentane were not included in the development of the functional form but were used to test the transferability to other fluids. The polar form was used for the refrigerants trichlorofluoromethane (R-11), dichlorodifluoromethane (R-12), chlorodifluoromethane (R-22), difluoromethane (R-32), 1,1,2-trichloro-1,2,2-trifluoroethane (R-113), 2,2-dichloro-1,1,1-trifluoroethane (R-123), pentafluoroethane (R-125), 1,1,1,2-tetrafluoroethane (R-134a), 1,1,1-trifluoroethane (R-143a), and 1,1-difluoroethane (R-152a) along with the fluids ethylene, carbon dioxide, and ammonia. The data sets for R-11 and R-113 were not included in the development of the functional form but were also used to test the transferability to other fluids for the polar form. The new form was able to represent the properties of the polar fluid ammonia; however, attempts to describe water as well with these equations were unsuccessful, probably due to the strong effects of association.

Uncertainties of calculated properties from the equations reported here are somewhat greater than those of state-of-the-art measurements of the specific properties. The 12-parameter Span and Wagner equations fulfill the accuracy requirements of most technical applications and show the desired numerical stability. Table 1 lists the target uncertainty levels of these equations, with higher uncertainties expected in the critical region (which is generally within 30 % of the critical density and up to 5 % of the critical temperature). Data at pressures above 100 MPa were not always considered due to their very limited technical importance. The uncertainties given in Table 1 were used as guides in this work. However, not all of the equations could be fitted within these limits due to higher uncertainties in the measurements for particular fluids. In general, accurate thermal data ($p\rho T$ in the liquid and second virial coefficients for the vapor) over various areas of the fluid surface along with vapor pressures were required for each fluid to obtain the desired uncertainties. The availability of caloric information for a particular fluid decreased the uncertainties in the final equations. All of the equations were constrained (i.e., by fixing the first and second derivatives of pressure with respect to density to be near zero at the selected critical point) such that the calculated critical temperature is within 0.01 K of the selected critical temperature. The success of the equations of

Table 2. Summary of Critical Points (reducing parameters)

fluid	critical temperature (T_c/K)	critical pressure[a] (p_c/MPa)	critical density (ρ_c/mol·dm^{-3})	source
acetone	508.1	4.70	4.70	this work
carbon monoxide	132.86	3.494	10.85	Goodwin (1985)
carbonyl sulfide	378.77	6.37	7.41	Robinson and Senturk (1979a)
decane	617.7	2.103	1.64	Lemmon and Goodwin (2000)
hydrogen sulfide	373.1	9.000	10.19	this work
isopentane	460.35	3.378	3.271	Das et al. (1977)
neopentane	433.74	3.196	3.27	this work
isohexane	497.7	3.04	2.715	Daubert (1996)
krypton	209.48	5.525	10.85	this work
nitrous oxide	309.52	7.245	10.27	this work
nonane	594.55	2.281	1.81	Lemmon and Goodwin (2000)
sulfur dioxide	430.64	7.884	8.195	this work
toluene	591.75	4.126	3.169	Tsonopoulos and Ambrose (1995)
xenon	289.733	5.842	8.40[b]	Gillis et al. (2004)
R-116	293.03	3.048	4.444	this work
R-141b	477.5	4.212	3.921	Duarte-Garza et al. (1997)
R-142b	410.26	4.055	4.438	Tanikawa et al. (1992)
R-218	345.02	2.640	3.34	Brown (1963)
R-245fa	427.16	3.651	3.85	Grebenkov et al. (2004)
R-41	317.28	5.897	9.30	Magee (1998)

[a] The critical pressure was obtained from the value calculated with the equation of state at the critical temperature and density of the fluid. [b] The critical density for xenon was determined in this work.

state presented here demonstrates the utility of the fixed functional form in assessing the quality of the data.

Functional Form of the Equation of State

Critical and Triple Points. The temperature and density values at the critical point are two of the most important properties required in the development of equations of state, especially in equations such as those of this work that use generalized terms. However, measurements of the critical point are often scarce and vary widely between sources. Additionally, there are fewer measurements of the critical density than of the critical temperature. The critical density is particularly difficult to determine accurately by experiment because of the infinite compressibility at the critical point. For nonane and decane, the critical temperature approaches the onset of dissociation, thus increasing the uncertainties in experimental values. However, several methods have been used to fit temperature, pressure, or density as a function of the alkane number. The method used here for the critical temperature and pressure of nonane and decane was published in previous work (Lemmon and Goodwin, 2000). Ambrose and Tsonopoulos (1995) and Daubert (1996) reported additional information on recommended values for the critical properties of normal and branched alkanes.

The critical parameters and sources for the fluids described in this work are listed in Table 2. In general, reasonable or recommended values were selected from the literature. Since the short equation of state is not intended for accurate properties in the critical region, small changes in the critical values have minimal impact on the accuracies of the equations. For some cases, the critical values were determined from available saturated density data with the use of power law equations:

$$\frac{\rho_\sigma}{\rho_c} - 1 = N_1\left(1 - \frac{T_\sigma}{T_c}\right) \pm N_2\left(1 - \frac{T_\sigma}{T_c}\right)^\beta \tag{1}$$

where T_c is the critical temperature, ρ_c is the critical density, N_1, N_2, and β are fitted parameters, T_σ is the saturation temperature, and ρ_σ is the saturation density for the liquid or the vapor; see, for example, Ley-Koo and Sengers (1982). This equation is valid only in the critical region. A list of all symbols used in this paper is given in Table 3.

The critical temperature and critical density (from Table 2) for some fluids were fitted simultaneously with the coefficients of the equation of state. The critical pressures for each fluid were generally determined from calculations with the equation of state at the critical temperature and density. The values of the critical parameters reported in Table 2 should be used for all property calculations from the equations of state reported here.

The selected triple point temperatures and their sources are reported in Table 4 along with values for the normal boiling point temperature and the acentric factor, both calculated from the equation of state. The molar masses given in Table 4 were determined from the atomic weights of the elements given by Coplen (2001). The standard atomic weight of krypton was changed from 83.80 ± 0.01 to 83.798 ± 0.002 based on the work of Aregbe et al. (2001) as accepted by IUPAC as a standard in Loss (2003). Table 4 also gives the upper temperature and pressure limits for each equation.

Equation of State. The equation of state expressed in a fundamental form explicit in the Helmholtz energy has become the most widely used method for calculating thermodynamic properties with high accuracy for many fluids. The independent variables in the functional form are density and temperature:

$$a(\rho,T) = a^0(\rho,T) + a^r(\rho,T) \tag{2}$$

where $a(\rho,T)$ is the Helmholtz energy, $a^0(\rho,T)$ is the ideal gas contribution to the Helmholtz energy, and $a^r(\rho,T)$ is the residual Helmholtz energy that results from intermolecular forces. All thermodynamic properties can be calculated as derivatives of the Helmholtz energy. For example, the pressure derived from this expression is

$$p = \rho^2\left(\frac{\partial a}{\partial \rho}\right)_T \tag{3}$$

In practical applications, the used functional form is the dimensionless Helmholtz energy, α, as a function of a dimensionless density and temperature. The form of this equation is

$$\frac{a(\rho,T)}{RT} = \alpha(\delta,\tau) = \alpha^0(\delta,\tau) + \alpha^r(\delta,\tau) \tag{4}$$

where $\delta = \rho/\rho_c$ and $\tau = T_c/T$.

Table 3. List of Symbols

symbol	physical quantity	specific units[a]	molar units[a]
a	Helmholtz energy	$\mathrm{J \cdot kg^{-1}}$	$\mathrm{J \cdot mol^{-1}}$
B	second virial coefficient	$\mathrm{m^3 \cdot kg^{-1}}$	$\mathrm{m^3 \cdot mol^{-1}}$
c_p	isobaric heat capacity	$\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
c_v	isochoric heat capacity	$\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
c_σ	saturated liquid heat capacity	$\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
g	Gibbs energy	$\mathrm{J \cdot kg^{-1}}$	$\mathrm{J \cdot mol^{-1}}$
h	enthalpy	$\mathrm{J \cdot kg^{-1}}$	$\mathrm{J \cdot mol^{-1}}$
M	molar mass (molecular weight)		
p	pressure	Pa	Pa
R	specific gas constant ($R = R_\mathrm{m}/M$)	$\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	
R_m	molar gas constant		$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
s	entropy	$\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
T	temperature (ITS-90)	K	K
u	internal energy	$\mathrm{J \cdot kg^{-1}}$	$\mathrm{J \cdot mol^{-1}}$
w	speed of sound	$\mathrm{m \cdot s^{-1}}$	$\mathrm{m \cdot s^{-1}}$
Z	compressibility factor ($Z = p/\rho RT$)		
α	reduced Helmholtz energy ($\alpha = a/RT$)		
δ	reduced density ($\delta = \rho/\rho_\mathrm{c}$)		
ρ	density	$\mathrm{kg \cdot m^{-3}}$	$\mathrm{mol \cdot m^{-3}}$
τ	inverse reduced temperature ($\tau = T_\mathrm{c}/T$)		
	Superscripts		
0	ideal gas property		
r	residual		
	Subscripts		
0	reference state property		
c	critical point property		
calc	calculated using an equation		
data	experimental value		
trp	triple point property		
σ	saturation property		

[a] To change from specific to molar properties, the specific gas constant, R, must be replaced by the universal molar gas constant, R_m, in the equations in this paper.

Table 4. Summary of Other Fixed Points and Ranges of the Equation of State

fluid	triple point temperature[a] (T/K)	boiling point temperature[b] (T/K)	molar mass (M)	acentric factor[b]	upper temperature limit (T/K)	upper pressure limit (p/MPa)
acetone	178.5	329.22	58.07914	0.3071	550	700
carbon monoxide	68.16	81.64	28.0101	0.0497	500	100
carbonyl sulfide	134.3	222.99	60.0751	0.0978	650	50
decane	243.5	447.27	142.28168	0.4884	675[c]	800
hydrogen sulfide	187.7	212.85	34.08088	0.1005	760	170
isopentane	112.65	300.98	72.14878	0.2274	500	1000
neopentane	256.6	282.65	72.14878	0.1961	550	200
isohexane	119.6	333.36	86.17536	0.2797	550	1000
krypton	115.77	119.73	83.798	−0.00089	750	200
nitrous oxide	182.33	184.68	44.0128	0.1613	525	50
nonane	219.7	423.91	128.2551	0.4433	600	800
sulfur dioxide	197.7	263.13	64.0638	0.2557	525	35
toluene	178.0	383.75	92.13842	0.2657	700	500
xenon	161.4	165.05	131.293	0.00363	750	700
R-116	173.1	195.06	138.01182	0.2566	425	50
R-141b	169.68	305.20	116.94962	0.2195	500[c]	400
R-142b	142.72	264.03	100.49503	0.2321	470	60
R-218	125.45	236.36	188.01933	0.3172	440	20
R-245fa	171.05	288.29	134.04794	0.3776	440	200
R-41	129.82	194.84	34.03292	0.2004	425	70

[a] Acetone: Wilhoit et al. (1985). CO: Staveley et al. (1981). COS: Clusius and Weigand (1940). Decane: Finke et al. (1954). H_2S: Cubitt et al. (1987). Isopentane: Parks and Huffman (1931). Neopentane: Hoepfner et al. (1979). Isohexane: Douslin and Huffman (1946). Krypton: Staveley et al. (1981). N_2O: Machado et al. (1980). Nonane: Finke et al. (1954). SO_2: Giauque and Stephenson (1938). Toluene: Ziegler and Andrews (1942). Xenon: Kemp et al. (1985). R-116: Pace and Aston (1948). R-141b: Henne and Plueddeman (1943). R-142b: Blanke and Weiss (1991). R-218: Pace and Plaush (1967). R-245fa: Beyerlein et al. (1993). R-41: Duarte-Garza and Magee (1999). [b] Calculated from the equations of state reported in this work. [c] The upper temperature limit has been set higher than the onset of decomposition of the fluid.

Properties of the Ideal Gas. The Helmholtz energy of the ideal gas is given by

$$a^0 = h^0 - RT - Ts^0 \tag{5}$$

The ideal gas enthalpy is given by

$$h^0 = h_0^0 + \int_{T_0}^{T} c_p^0 \, \mathrm{d}T \tag{6}$$

where c_p^0 is the ideal gas isobaric heat capacity. The ideal gas entropy is given by

$$s^0 = s_0^0 + \int_{T_0}^{T} \frac{c_p^0}{T} \, \mathrm{d}T - R \ln\left(\frac{\rho T}{\rho_0 T_0}\right) \tag{7}$$

where T_0 and p_0 are arbitrary constants and ρ_0 is the ideal gas density at T_0 and p_0, $\rho_0 = p_0/T_0R$. Combining these equations results in the following expression for the Helmholtz energy of the ideal gas:

$$a^0 = h_0^0 + \int_{T_0}^{T} c_p^0 \, \mathrm{d}T - RT - T\left[s_0^0 + \int_{T_0}^{T} \frac{c_p^0}{T}\mathrm{d}T - R\ln\left(\frac{\rho T}{\rho_0 T_0}\right)\right] \qquad (8)$$

The ideal gas Helmholtz energy is given in a dimensionless form by

$$\alpha^0 = \frac{h_0^0 \tau}{RT_\mathrm{c}} - \frac{s_0^0}{R} - 1 + \ln\frac{\delta\tau_0}{\delta_0\tau} - \frac{\tau}{R}\int_{\tau_0}^{\tau}\frac{c_p^0}{\tau^2}\mathrm{d}\tau + \frac{1}{R}\int_{\tau_0}^{\tau}\frac{c_p^0}{\tau}\mathrm{d}\tau \qquad (9)$$

where $\delta_0 = \rho_0/\rho_\mathrm{c}$ and $\tau_0 = T_\mathrm{c}/T_0$. The arbitrary values for h_0^0 and s_0^0 are chosen based on common convention in a particular industry or according to the recommendations of the International Union for Pure and Applied Chemistry (IUPAC). For refrigerants, the enthalpy and entropy of the saturated liquid state at 0 °C are respectively set at 200 $\mathrm{kJ{\cdot}kg^{-1}}$ and 1 $\mathrm{kJ{\cdot}kg^{-1}{\cdot}K^{-1}}$. For hydrocarbons, the enthalpy and entropy are often set to zero for the liquid at the normal boiling point. Other industries use a similar convention setting the enthalpy and entropy to zero at −40 °C.

The calculation of thermodynamic properties from the ideal gas Helmholtz energy requires an equation for the ideal gas isobaric heat capacity, c_p^0. These equations are usually derived by fitting values of heat capacity measurements extrapolated to zero pressure, gaseous speed of sound measurements, or calculations from statistical methods using spectroscopically determined frequencies. Differences between various theoretical values arise from the use of different approximations to calculate the various couplings between the vibrational modes of the molecule. For many of the fluids of interest here, there is little information on the ideal gas heat capacity, especially at temperatures outside the range (250 to 350) K. However, values calculated from statistical techniques are available from Marsh et al. (1994) for temperatures as low as 50 K and as high as 5000 K. These values were included in the fitting of c_p^0 for most of the fluids presented here, with comparisons made to all experimental or calculated information to verify the accuracy of the ideal gas equations. Heat capacities for all of the fluids were fitted to the same functional form:

$$\frac{c_p^0}{R_\mathrm{m}} = c_0 + c_1(T/\mathrm{K})^{c_2} + \sum_{k=1}^{5}\upsilon_k\left(\frac{u_k}{T}\right)^2\frac{\exp(u_k/T)}{[\exp(u_k/T) - 1]^2} \qquad (10)$$

where the molar gas constant, R_m, is 8.314472 $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$ (Mohr and Taylor, 1999). Only four of the fluids used the second term (which contains c_1 and c_2) due to the larger temperature dependence in the ideal gas heat capacity of the substance. The Einstein functions containing the coefficients υ_k were used so that the temperature dependence of the ideal gas heat capacity would be similar to that derived from statistical methods. However, the u_k values are empirical coefficients and should not be confused with the vibrational frequencies. For nonane, the increase in the heat capacity between (0 and 100) K from 4 R (contributions from translation and rotation are fully excited) to 17.3 R was not modeled (as indicated by the value of c_0). Likewise, for decane, the increase between (0 and 130) K from 4 R to approximately 19 R was also not fitted.

The ideal gas Helmholtz energy equation, derived from eqs 9 and 10, is

$$\alpha^0 = a_1 + a_2\tau + \ln\delta + (c_0 - 1)\ln\tau - \frac{c_1(T_\mathrm{c}/\mathrm{K})^{c_2}}{c_2(c_2+1)}\tau^{-c_2} + \sum_{k=1}^{5}\upsilon_k\ln[1 - \exp(-u_k\tau/T_\mathrm{c})] \qquad (11)$$

where a_1 and a_2 are determined to correspond with the values of h_0^0 and s_0^0 defined above. Coefficients for the Einstein terms are given in Table 5, and values of a_1, a_2, c_0, c_1, and c_2 are given in Table 6. Additional digits are reported for a_1 and a_2 beyond those required to obtain the stated uncertainties in the equations so as to give better representation of the enthalpy and entropy at the state point defined by the reference state, described earlier after eq 9. This is particularly important when the enthalpy and entropy have been set to zero at the reference state, such as that for the saturated liquid at the normal boiling point for the hydrocarbons.

Properties of the Real Fluid. The behavior of the residual (or real) fluid is described using empirical models that are only loosely tied to theoretical information such as the second and third virial coefficients. Although the models are consistent with all of the known fluid-phase thermodynamic behavior (except in the asymptotic critical region), the coefficients of the equations depend mostly on the experimental data representing the thermodynamic properties of each fluid.

The common functional form used for the Helmholtz energy equation of state is

$$\alpha^\mathrm{r}(\delta,\tau) = \sum N_k\delta^{i_k}\tau^{j_k} + \sum N_k\delta^{i_k}\tau^{j_k}\exp(-\delta^{l_k}) \qquad (12)$$

where each summation typically contains 4 to 20 terms and where the index k points to each individual term (see Span, 2000, or Jacobsen et al., 2000). Although the values of i_k, j_k, and l_k are arbitrary, the j_k are generally expected to be greater than zero, and i_k and l_k are integers greater than zero. As discussed in the Introduction, the work of Span and Wagner (2003a−c) resulted in two equations, each with 12 terms that can be used to represent the thermodynamic properties of polar or nonpolar fluids. The equation for nonpolar (or weakly polar) fluids was applied here to carbon monoxide, carbonyl sulfide, decane, hydrogen sulfide, 2-methylbutane (isopentane), 2-methylpentane (isohexane), 2,2-dimethylpropane (neopentane), krypton, nonane, toluene, xenon, and hexafluoroethane (R-116). The functional form is

$$\begin{aligned}\alpha^\mathrm{r}(\delta,\tau) = {} & n_1\delta\tau^{0.25} + n_2\delta\tau^{1.125} + n_3\delta\tau^{1.5} + n_4\delta^2\tau^{1.375} + \\ & n_5\delta^3\tau^{0.25} + n_6\delta^7\tau^{0.875} + n_7\delta^2\tau^{0.625}\exp^{-\delta} + n_8\delta^5\tau^{1.75}\exp^{-\delta} + \\ & n_9\delta\tau^{3.625}\exp^{-\delta^2} + n_{10}\delta^4\tau^{3.625}\exp^{-\delta^2} + n_{11}\delta^3\tau^{14.5}\exp^{-\delta^3} + \\ & n_{12}\delta^4\tau^{12.0}\exp^{-\delta^3}\end{aligned} \qquad (13)$$

The equation for polar fluids was applied here to acetone, nitrous oxide, sulfur dioxide, 1,1-dichloro-1-fluoroethane (R-141b), 1-chloro-1,1-difluoroethane (R-142b), octafluoropropane (R-218), 1,1,1,3,3-pentafluoropropane (R-245fa), and fluoromethane (R-41). The functional form is

$$\begin{aligned}\alpha^\mathrm{r}(\delta,\tau) = {} & n_1\delta\tau^{0.25} + n_2\delta\tau^{1.25} + n_3\delta\tau^{1.5} + n_4\delta^3\tau^{0.25} + \\ & n_5\delta^7\tau^{0.875} + n_6\delta\tau^{2.375}\exp^{-\delta} + n_7\delta^2\tau^{2.0}\exp^{-\delta} + \\ & n_8\delta^5\tau^{2.125}\exp^{-\delta} + n_9\delta\tau^{3.5}\exp^{-\delta^2} + n_{10}\delta\tau^{6.5}\exp^{-\delta^2} + \\ & n_{11}\delta^4\tau^{4.75}\exp^{-\delta^2} + n_{12}\delta^2\tau^{12.5}\exp^{-\delta^3}\end{aligned} \qquad (14)$$

Table 5. Coefficients of the Einstein Terms in the Ideal Gas Heat Capacity Equations

fluid	v_1	u_1/K	v_2	u_2/K	v_3	u_3/K	v_4	u_4/K
acetone	3.7072	310.0	7.0675	3480.0	11.012	1576.0		
carbon monoxide	1.0128	3089.0						
carbonyl sulfide	2.1651	768.0	0.93456	1363.0	1.0623	3175.0	0.34269	12829.0
decane	25.685	1193.0	28.233	2140.0	12.417	4763.0	10.035	10862.0
hydrogen sulfide	1.1364	1823.0	1.9721	3965.0				
isopentane	7.4056	442.0	9.5772	1109.0	15.765	2069.0	12.119	4193.0
neopentane	14.422	710.0	12.868	1725.0	17.247	3280.0	12.663	7787.0
isohexane	7.9127	325.0	16.871	1150.0	19.257	2397.0	14.075	5893.0
krypton								
nitrous oxide	2.1769	879.0	1.6145	2372.0	0.48393	5447.0		
nonane	24.926	1221.0	24.842	2244.0	11.188	5008.0	17.483	11724.0
sulfur dioxide	1.0620	775.0	1.9401	1851.0				
toluene[a]	1.6994	190.0	8.0577	797.0	17.059	1619.0	8.4567	3072.0
xenon								
R-116	2.4818	190.0	7.0622	622.0	7.9951	1470.0		
R-141b	6.8978	502.0	7.8157	1571.0	3.2039	4603.0		
R-142b	5.0385	473.0	6.8356	1256.0	4.0591	2497.0	2.8136	6840.0
R-218	7.2198	326.0	7.2692	595.0	11.599	1489.0		
R-245fa	5.5728	222.0	10.385	1010.0	12.554	2450.0		
R-41	5.6936	1841.0	2.9351	4232.0				

[a] v_5 and u_5 of toluene are 8.6423 and 7915.0 K, respectively.

The coefficients n_k of the residual part of the equation of state are given in Table 7 for the fluids that use the nonpolar form and in Table 8 for the fluids that use the polar form. The ranges of validity of the formulations are given in Table 4.

The functions used for calculating pressure (p), compressibility factor (Z), internal energy (u), enthalpy (h), entropy (s), Gibbs energy (g), isochoric heat capacity (c_v), isobaric heat capacity (c_p), and the speed of sound (w) from the reduced Helmholtz energy equation are given in the equations below:

$$Z = \frac{p}{\rho RT} = 1 + \delta\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \delta}\right)_{\tau} \tag{15}$$

$$\frac{u}{RT} = \tau\left[\left(\frac{\partial \alpha^{0}}{\partial \tau}\right)_{\delta} + \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \tau}\right)_{\delta}\right] \tag{16}$$

$$\frac{h}{RT} = \tau\left[\left(\frac{\partial \alpha^{0}}{\partial \tau}\right)_{\delta} + \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \tau}\right)_{\delta}\right] + \delta\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \delta}\right)_{\tau} + 1 \tag{17}$$

$$\frac{s}{R} = \tau\left[\left(\frac{\partial \alpha^{0}}{\partial \tau}\right)_{\delta} + \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \tau}\right)_{\delta}\right] - \alpha^{0} - \alpha^{\mathrm{r}} \tag{18}$$

$$\frac{g}{RT} = 1 + \alpha^{0} + \alpha^{\mathrm{r}} + \delta\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \delta}\right)_{\tau} \tag{19}$$

$$\frac{c_v}{R} = -\tau^2\left[\left(\frac{\partial^2 \alpha^{0}}{\partial \tau^2}\right)_{\delta} + \left(\frac{\partial^2 \alpha^{\mathrm{r}}}{\partial \tau^2}\right)_{\delta}\right] \tag{20}$$

$$\frac{c_p}{R} = \frac{c_v}{R} + \frac{\left[1 + \delta\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \delta}\right)_{\tau} - \delta\tau\left(\frac{\partial^2 \alpha^{\mathrm{r}}}{\partial \delta \partial \tau}\right)\right]^2}{\left[1 + 2\delta\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \delta}\right)_{\tau} + \delta^2\left(\frac{\partial^2 \alpha^{\mathrm{r}}}{\partial \delta^2}\right)_{\tau}\right]} \tag{21}$$

$$\frac{w^2}{RT} = 1 + 2\delta\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \delta}\right)_{\tau} + \delta^2\left(\frac{\partial^2 \alpha^{\mathrm{r}}}{\partial \delta^2}\right)_{\tau} - \frac{\left[1 + \delta\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \delta}\right)_{\tau} - \delta\tau\left(\frac{\partial^2 \alpha^{\mathrm{r}}}{\partial \delta \partial \tau}\right)\right]^2}{\tau^2\left[\left(\frac{\partial^2 \alpha^{0}}{\partial \tau^2}\right)_{\delta} + \left(\frac{\partial^2 \alpha^{\mathrm{r}}}{\partial \tau^2}\right)_{\delta}\right]} \tag{22}$$

Other derived properties, given below, include the first derivative of pressure with respect to density at constant temperature, $(\partial p/\partial \rho)_T$, the second derivative of pressure with respect to density at constant temperature, $(\partial^2 p/\partial \rho^2)_T$, and the first derivative of pressure with respect to temperature at constant density, $(\partial p/\partial T)_\rho$:

$$\left(\frac{\partial p}{\partial \rho}\right)_T = RT\left[1 + 2\delta\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \delta}\right)_{\tau} + \delta^2\left(\frac{\partial^2 \alpha^{\mathrm{r}}}{\partial \delta^2}\right)_{\tau}\right] \tag{23}$$

$$\left(\frac{\partial^2 p}{\partial \rho^2}\right)_T = \frac{RT}{\rho}\left[2\delta\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \delta}\right)_{\tau} + 4\delta^2\left(\frac{\partial^2 \alpha^{\mathrm{r}}}{\partial \delta^2}\right)_{\tau} + \delta^3\left(\frac{\partial^3 \alpha^{\mathrm{r}}}{\partial \delta^3}\right)_{\tau}\right] \tag{24}$$

$$\left(\frac{\partial p}{\partial T}\right)_\rho = R\rho\left[1 + \delta\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \delta}\right)_{\tau} - \delta\tau\left(\frac{\partial^2 \alpha^{\mathrm{r}}}{\partial \delta \partial \tau}\right)\right] \tag{25}$$

The publication of Lemmon et al. (2000) gives equations for additional thermodynamic properties such as the isothermal compressibility and the Joule−Thomson coefficient. The derivatives of the ideal gas Helmholtz energy and the residual Helmholtz energy required by the equations to calculate these thermodynamic properties are given in Span and Wagner (2003a−c).

Fitting Procedures. In the development of equations of state, various data types are useful in evaluating other types of data. Since one equation is used to represent multiple properties, the accuracy of one property can influence the behavior of another. In particular, the availability of heat capacity data is fundamental in equation of state development. Without it, equations can inadvertently give negative heat capacities at low temperatures or show unrealistic curvature in certain areas of the thermodynamic surface. Although the amount of heat capacity data for a fluid may be limited, even a few values in the liquid phase can often be sufficient to tie down the equation of state when working with a fixed functional form. This can be confirmed by plotting various constant properties lines over the surface of state, and by comparing the slopes of such lines to expected behavior. The extrapolation behavior of the functional form used here at low and high temperatures, pressures, and densities can give confidence in the equation of state in the absence of highly accurate experimental data over some areas of the thermodynamic surface.

Fitting the coefficients of the equation of state is a process of correlating selected experimental data with a model that is generally empirical in nature. In this work, the model was the fixed functional form which exhibits proper behavior in the ideal

Table 6. Coefficients Used in the Ideal Gas Heat Capacity and Helmholtz Energy Equations

fluid	c_0	c_1	c_2	a_1	a_2
acetone	4.0			−9.4883659997	7.1422719708
carbon monoxide	3.5	0.22311×10^{-6}	1.5	−3.3728318564	3.3683460039
carbonyl sulfide	3.5			−3.6587449805	3.7349245016
decane	19.109			13.9361966549	−10.5265128286
hydrogen sulfide	4.0	0.14327×10^{-5}	1.5	−4.0740770957	3.7632137341
isopentane	4.0			2.5822330405	1.1609103419
neopentane	4.0			0.8702452614	1.6071746358
isohexane	4.0			6.9259123919	−0.3128629679
krypton	2.5			−3.7506412806	3.7798018435
nitrous oxide	3.5			−4.4262736272	4.3120475243
nonane	17.349			10.7927224829	−8.2418318753
sulfur dioxide	4.0	0.72453×10^{-4}	1.0	−4.5328346436	4.4777967379
toluene	4.0			3.5241174832	1.1360823464
xenon	2.5			−3.8227178129	3.8416395351
R-116	4.0			−10.7088650331	8.9148979056
R-141b	4.0			−15.5074814985	9.1871858933
R-142b	4.0			−12.6016527149	8.3160183265
R-218	4.0			−15.6587335175	11.4531412796
R-245fa	4.0			−13.4283638514	9.8723653800
R-41	4.0	0.00016937	1.0	−4.8676441160	4.2527951258

Table 7. Coefficients of the Equation of State (eq 13) for Nonpolar or Weakly Polar Fluids

k	carbon monoxide	carbonyl sulfide	decane	hydrogen sulfide
1	0.90554	0.94374	1.0461	0.87641
2	−2.4515	−2.5348	−2.4807	−2.0367
3	0.53149	0.59058	0.74372	0.21634
4	0.024173	−0.021488	−0.52579	−0.050199
5	0.072156	0.082083	0.15315	0.066994
6	0.00018818	0.00024689	0.00032865	0.00019076
7	0.19405	0.21226	0.84178	0.20227
8	−0.043268	−0.041251	0.055424	−0.0045348
9	−0.12778	−0.22333	−0.73555	−0.22230
10	−0.027896	−0.050828	−0.18507	−0.034714
11	−0.034154	−0.028333	−0.020775	−0.014885
12	0.016329	0.016983	0.012335	0.0074154

k	isopentane	neopentane	isohexane	krypton
1	1.0963	1.1136	1.1027	0.83561
2	−3.0402	−3.1792	−2.9699	−2.3725
3	1.0317	1.1411	1.0295	0.54567
4	−0.15410	−0.10467	−0.21238	0.014361
5	0.11535	0.11754	0.11897	0.066502
6	0.00029809	0.00034058	0.00027738	0.00019310
7	0.39571	0.29553	0.40103	0.16818
8	−0.045881	−0.074765	−0.034238	−0.033133
9	−0.35804	−0.31474	−0.43584	−0.15008
10	−0.10107	−0.099401	−0.11693	−0.022897
11	−0.035484	−0.039569	−0.019262	−0.021454
12	0.018156	0.023177	0.0080783	0.0069397

k	nonane	toluene	xenon	R-116
1	1.1151	0.96464	0.83115	1.1632
2	−2.7020	−2.7855	−2.3553	−2.8123
3	0.83416	0.86712	0.53904	0.77202
4	−0.38828	−0.18860	0.014382	−0.14331
5	0.13760	0.11804	0.066309	0.10227
6	0.00028185	0.00025181	0.00019649	0.00024629
7	0.62037	0.57196	0.14996	0.30893
8	0.015847	−0.029287	−0.035319	−0.028499
9	−0.61726	−0.43351	−0.15929	−0.30343
10	−0.15043	−0.12540	−0.027521	−0.068793
11	−0.012982	−0.028207	−0.023305	−0.027218
12	0.0044325	0.014076	0.0086941	0.010665

gas and low density regions and extrapolates to temperatures and pressures higher than those defined by experiment. In all cases, experimental data are considered paramount, and the proof of validity for any equation of state is evidenced in its ability to represent the thermodynamic properties of the fluid generally within the uncertainty of the experimental values.

Table 8. Coefficients of the Equation of State (eq 14) for Polar Fluids

k	acetone	nitrous oxide	sulfur dioxide	R-41
1	0.90041	0.88045	0.93061	0.85316
2	−2.1267	−2.4235	−1.9528	−2.6366
3	−0.083409	0.38237	−0.17467	0.69129
4	0.065683	0.068917	0.061524	0.054681
5	0.00016527	0.00020367	0.00017711	0.00012796
6	−0.039663	0.13122	0.21615	−0.37093
7	0.72085	0.46032	0.51353	0.33920
8	0.0092318	−0.0036985	0.010419	−0.0017413
9	−0.17217	−0.23263	−0.25286	−0.095417
10	−0.14961	−0.00042859	−0.054720	−0.078852
11	−0.076124	−0.042810	−0.059856	−0.030729
12	−0.018166	−0.023038	−0.016523	−0.011497

k	R-141b	R-142b	R-218	R-245fa
1	1.1469	1.0038	1.3270	1.2904
2	−3.6799	−2.7662	−3.8433	−3.2154
3	1.3469	0.42921	0.92200	0.50693
4	0.083329	0.081363	0.11360	0.093148
5	0.00025137	0.00024174	0.00036195	0.00027638
6	0.32720	0.48246	1.1001	0.71458
7	0.46946	0.75542	1.1896	0.87252
8	−0.029829	−0.007430	−0.025147	−0.015077
9	−0.31621	−0.41460	−0.65923	−0.40645
10	−0.026219	−0.016558	−0.027969	−0.11701
11	−0.078043	−0.10644	−0.18330	−0.13062
12	−0.020498	−0.021704	−0.021630	−0.022952

Nonlinear fitting techniques were used to fit the coefficients of the equations. The selected data used in fitting were a subset of the available database determined by the correlator to be representative of the most accurate values measured. The nonlinear algorithm adjusted the coefficients of the equation of state to reduce the overall sum of squares of the deviations of calculated properties from the input data. Each data point was individually weighted according to type, region, and uncertainty. Additionally, the values of the first and second derivatives of pressure with respect to density were fitted to be near zero at the selected critical point. The final set of coefficients for each equation represented not only the fitted data but also the consistent data available for each fluid.

Experimental Data and Comparisons to the Equations of State

The units adopted for this work were kelvins (ITS-90) for temperature, megapascals for pressure, and moles per cubic decimeter for density. The units of the experimental data were converted as necessary from those in the original publications to these units. Where necessary, temperatures reported on IPTS-68 and IPTS-48 were converted to the International Temperature Scale of 1990 (ITS-90) (Preston-Thomas, 1990).

Much of the experimental data reported in the literature for the hydrocarbons were measured over 50 years ago, with measurements for some of the fluids being made as far back as the 1800s. On the other hand, most of the measurements for the refrigerants were made during the last 15 years. However, in many cases, the year of publication cannot be correlated with the uncertainties in the data. For many of the hydrocarbons, there are numerous publications on the vapor pressure at its boiling point and on the saturated liquid density of the fluid at 298.15 K. However, the development of equations of state considers multiple data types, including $p\rho T$, saturation properties, critical parameters, heat capacities, sound speeds, second virial coefficients, and ideal gas isobaric heat capacities. In addition, measurements must be available over a wide area of the fluid surface in order to develop accurate equations. Often, only selected data from among the available data are used in fitting, although comparisons are made to all available experimental data, including those not used in the development of the equation of state, to estimate the uncertainties in the equations (where the uncertainties can be considered as estimates of a combined expanded uncertainty with a coverage factor of 2). These values are determined by statistical comparisons of property values calculated from the equation of state to experimental data. The deviation in any property, X, is defined here as

$$\Delta X = \frac{X_{\text{data}} - X_{\text{calc}}}{X_{\text{data}}} \tag{26}$$

and the average absolute deviation is defined as

$$\text{AAD} = \frac{1}{n}\sum_{i=1}^{n}|\Delta X_i| \tag{27}$$

where n is the number of data points. Statistical information on the deviations between the equations of state and experimental data is given in Table 9 for six regions. These regions include the liquid and gas phases at subcritical temperatures, the extended critical region defined as $0.98 < T/T_c < 1.1$ and $0.7 < \rho/\rho_c < 1.4$, and states at supercritical temperatures outside of the extended critical region. The supercritical region is subdivided into a low-density range (LD, $\rho/\rho_c < 0.6$), a medium-density range (MD, $0.6 < \rho/\rho_c < 1.5$), and a high-density range (HD, $\rho/\rho_c > 1.5$). The average absolute deviations in Table 9 do not include data points with pressures greater than 100 MPa, although these data points are shown in the figures. Data obtained from the open literature with only one or two data points were not included in Table 9 unless the data point(s) were important to the development of the equation of state. Their inclusion would have more than doubled the number of references. However, these extra measurements are shown in the figures and are labeled as "Other data sets". In some of the figures that contain a substantial number of sources, data sets with limited data or data with high uncertainties are also included under the label "Other data sets". Density data are separated into "quasi isotherms" with temperature increments of about 10 K outside of the critical region; the temperatures listed at the top of each small plot are the lower bounds of the data in the plot. Data points shown at the upper or lower vertical limits of the graph indicate that the points are off scale. Data points for heat capacities and sound speeds are assumed to be in the liquid phase unless otherwise indicated. In the text below, discussions of maximum errors or of systematic offsets use the absolute values of the deviations.

Acetone. Experimental measurements for acetone and their deviations from the equation of state are summarized in Table 9 and shown in Figures 1 and 2. Between (280 and 320) K, there is a substantial amount of $p\rho T$ data for acetone in the liquid phase, particularly along the saturation line. At higher or lower temperatures, the amount and quality of data decrease rapidly. At 293 K and 298 K, the equation of state was fitted to the concentrated grouping of saturated liquid-phase densities so that most of the data fall within 0.2 % of the equation. Of the 100 saturated liquid density points near 298 K, 90 are within 0.2 %, 83 are within 0.1 %, and 50 are within 0.05 %. Below 270 K, there are several sets for which the equation deviates by 0.25 %. However, the data with these higher deviations come from three main sources: Archibald and Ure (1924), Felsing and Durban (1926), and Yergovich et al. (1971). These data sets show offsets of 0.25 % above 270 K as well, in poor agreement with the many other sources available at these higher temperatures. The data at the low temperatures were not fitted in order to decrease the deviations from the equation of state, rather the constant offset of 0.25 % was maintained throughout. There are only three data sets above 330 K for the saturated liquid phase, and the data in these sets show high scatter among themselves and systematic offsets from the equation of state. Above 430 K, the data of Campbell and Chatterjee (1968) show positive deviations, while the data of Tugarev et al. (1975) show negative deviations. The situation in the single-phase liquid is not much better. At temperatures from (270 to 370) K, deviations are typically within 0.5 %, with deviations of 0.1 % at 298 K for the data of Newitt and Weale (1951) and of Papaioannou et al. (1991). The data of Poehler and Kiran (1997) are in agreement with the equation at lower temperatures, but the equation deviates by 1 % from these data at 420 K. Attempts to fit these data caused systematic deviations in other properties, and it is unclear whether the equation or the data are in error. Above 500 K, the data of Keller and Stiel (1977) agree to within 0.5 % in density. The equation shows large systematic offsets from the data of Anderson et al. (1968) in the vapor phase. Many attempts were made to bring the equation into conformity with these data, but none was successful. Anderson et al. described in their paper a change of color in their sample at the upper temperature limit of their data, and it is not known how this change affected the data at lower temperatures. Additional measurements are required to verify the accuracy of the equation of state in the vapor phase.

Similar to the saturated liquid density, measurements of vapor pressure for acetone are quite plentiful in a limited region. Specifically, between (280 and 330) K, many of the experimental points are represented by the equation of state to within 0.2 %. However, there are many points that show deviations of up to 1.5 %, and there are a few additional data points with deviations greater than 1.5 %. The large scatter in these data introduce additional uncertainties into the equation, although the more recent data of Lee and Hu (1995), Muthu et al. (1983), Olivares Fuentes et al. (1983), and Olson (1981) indicate that the uncertainty in the equation is about 0.25 % between (290 and 390) K. The scatter increases below 290 K (e.g., at 260 K, the data of Ambrose et al. (1974) and of Hoepfner and Hostermann (1976) differ by 1 %). Additional high-accuracy measurements are needed at lower temperatures. Likewise, above 400 K, the scatter in the data increases up to 2 %, although

Table 9. Summary and Comparisons of Experimental Data[a]

		temp and pressure ranges		average absolute deviations (AAD/%)^b					
							supercritical fluid		
reference	no.	T/K	p/MPa	gas	liq	crit reg	LD	MD	HD
Acetone									
pρT Data									
Anderson et al. (1968)	74	298−423	0−0.72	2.79					
Bridgman (1913)	17	293−353	0.10−98.1		0.35				
Gupta and Hanks (1977)	24	273−363	2.76−22.1		0.31				
Keller and Stiel (1977)	54	507−538	9.36−36.9		0.16				0.17
Laesecke (2006)	35	278−318	0.08		0.11				
Newitt and Weale (1951)	6	298	40.5−91.2		0.08				
Papaioannou et al. (1991)	11	293−298	0.10−33.8		0.03				
Poehler and Kiran (1997)	56	323−423	1.65−64.9		0.43				
Vapor Pressures									
Ambrose et al. (1974)	46	259−508	0−4.70	0.31					
Archibald and Ure (1927)	24	179−293	0−0.02	46.4					
Beare et al. (1930)	4	293−308	0.02−0.05	0.27					
Boublik and Aim (1972)	15	260−328	0−0.10	0.30					
Campbell and Chatterjee (1968)	30	375−505	0.38−4.58	1.73					
Diaz Peña et al. (1978)	4	308−323	0.05−0.08	0.07					
Dragoescu et al. (1998)	4	298−313	0.03−0.06	0.37					
Dreisbach and Shrader (1949)	3	306−329	0.04−0.10	0.22					
Drucker et al. (1915)	32	179−262	0	21.6					
Felsing and Durban (1926)	32	204−339	0−0.14	3.37					
Hoepfner and Hostermann (1976)	17	215−293	0−0.02	1.06					
Jacob (1924)	9	253−293	0−0.02	2.01					
Kobe et al. (1955)	26	361−500	0.28−4.16	1.28					
Lee and Hu (1995)	6	343−363	0.16−0.29	0.17					
Maher and Smith (1980)	4	277−387	0.01−0.52	0.15					
Matvienko and Yarym-Agaev (1994)	5	273−313	0−0.05	4.60					
Muthu et al. (1983)	6	293−387	0.02−0.53	0.15					
Olivares Fuentes et al. (1983)	18	295−322	0.03−0.08	0.11					
Olson (1981)	9	293−333	0.02−0.12	0.13					
Othmer and Morley (1946)	5	330−432	0.10−1.38	1.12					
Radulescu and Alexa (1938)	5	273−293	0−0.02	0.43					
Roland (1928)	8	273−329	0−0.10	0.38					
Rosenbaum (1951)	9	446−505	1.72−4.48	0.45					
Sameshima (1918)	10	278−323	0.01−0.08	0.46					
Schmidt (1926)	5	273−308	0−0.05	1.37					
Schulze (1921)	4	273−328	0−0.10	0.69					
Sokolov et al. (1963)	21	279−329	0.01−0.10	0.75					
Taylor (1900)	46	294−329	0.03−0.10	1.24					
Tugarev et al. (1975)	16	348−507	0.18−4.66	0.75					
Zmaczynski (1930)	11	308−367	0.05−0.31	0.14					
Saturated Liquid Densities									
Archibald and Ure (1924)	10	183−273			0.31				
Bhagwat and Subnis (1948)	5	303−323			0.33				
Bramley (1916)	6	273−323			0.13				
Campbell and Chatterjee (1968)	33	375−507			0.58	5.68			
Casas et al. (2002)	3	288−308			0.02				
Costas and Patterson (1985)	3	283−313			0.19				
Deshpande and Bhatgadde (1968)	3	298−318			0.04				
Dizechi and Marschall (1982)	5	293−323			0.11				
Estrada-Baltazar et al. (2003)	9	283−323			0.05				
Faust (1912)	13	260−323			0.74				
Felsing and Durban (1926)	15	183−325			0.26				
French (1989)	7	278−323			0.06				
Hafez and Hartland (1976)	4	293−318			0.04				
Howard and Pike (1959)	4	293−323			0.09				
Kinart et al. (2002)	5	291−308			0.17				
Kumar (2000)	6	288−338			2.62				
Low and Moelwyn-Hughes (1962)	7	253−308			0.05				
McLure and Pegg (1996)	7	288−323			0.09				
Price (1919)	4	293−323			0.04				
Qin et al. (1992)	5	293			0.15				
Sears et al. (1956)	9	223−298			0.20				
Shakhova and Braude (1963)	6	218−293			0.08				
Terent'eva et al. (1973)	6	223−273			0.16				
Tugarev et al. (1975)	16	348−507			0.86	0.35			
Yergovich et al. (1971)	11	183−283			0.28				
Saturated Vapor Densities									
Campbell and Chatterjee (1968)	33	375−507		15.5		0.39			
Herz and Neukirch (1923)	4	486−508		15.9					
Isobaric Heat Capacities									
Collins et al. (1949)	12	332−438	0.10	0.97					
Costas and Patterson (1985)	3	283−313	0.02−0.06		0.80				
Deshpande and Bhatgadde (1971)	3	298−318	0.03−0.07		4.70				
Kelley (1929)	14	180−297	0−0.03		0.75				
Low and Moelwyn-Hughes (1962)	7	253−308	0−0.05		0.79				
Parks and Kelley (1928)	10	193−289	0−0.02		0.70				
Pennington and Kobe (1957)	14	338−439	0.03−0.17	0.17					
Staveley et al. (1955)	10	288−324	0.02−0.08		3.03				
Vilcu and Coman (1975)	10	330−420	0.10	2.16					
Williams and Daniels (1925)	3	293−313	0.02−0.06		4.28				
Yu et al. (1996)	5	372−515	0.10	4.32			0.56		
Speeds of Sound									
Casas et al. (2002)	3	288−308	0.02−0.05		0.20				
Deshpande and Bhatgadde (1968)	3	298−318	0.03−0.07		0.44				
Freyer et al. (1929)	6	273−323	0−0.08		0.45				
Krishnan (1941)	3	300	0.10		1.14				
Kumar (2000)	6	288−338	0.02−0.14		13.0				
Laesecke (2006)	33	278−318	0.08		0.13				
Low and Moelwyn-Hughes (1962)	7	253−308	0−0.05		0.29				
Nath and Tripathi (1983)	3	298−308	0.03−0.05		0.16				

Enthalpies of Vaporization																			
Belousov et al. (1964)	3	251−313		0.97						Yerlett and Wormald (1986)	8	373−505		1.71					
Pennington and Kobe (1957)	5	300−345		0.09															
Enthalpy Differences																			
Yerlett and Wormald (1986)	203	373−623	0.10−11.9	0.35			0.74												
Second Virial Coefficients																			
Anderson et al. (1968)	6	298−423		22.7						Olf et al. (1989)	4	393−433		1.11					
Bottomley and Spurling (1967)	14	305−431		2.19						Pennington and Kobe (1957)	5	300−345		3.16					
Dragoescu et al. (1999)	4	298−313		0.55						Spiske and Gaube (1987)	3	353−394		3.04					
Eucken and Meyer (1929)	6	342−374		39.2						Zaalishvili and Belousova (1964)	6	333−383		9.97					
Hajjar et al. (1969)	11	313−473		2.87						Zaalishvili and Kolysko (1960)	3	323−343		6.76					
Knoebel and Edmister (1968)	4	313−373		2.09						Zhang et al. (1966)	4	353−403		7.21					
Lambert et al. (1949)	12	292−406		11.5															
Ideal Gas Isobaric Heat Capacities																			
Ding et al. (1997)	3	410−631		0.25			0.03			Pennington and Kobe (1957)	4	338−439		0.07					
Marsh et al. (1994)^c	117	180−5000		0.33			0.74			Vilcu and Coman (1975)	10	330−420		3.55					
Carbon Monoxide																			
pρT Data																			
Barreiros et al. (1982b)	100	81.6−125	1.98−99.8		0.11					Michels et al. (1952a)	229	273−423	1.88−99.6				0.11	0.11	0.29
Bartlett et al. (1930)	117	203−473	0.10−81.1				0.26	0.35	0.18	Robertson and Babb (1970)	0		>100 MPa						
Goig (1929)	90	273	4.05−13.2				10.4			Scott (1929)	18	298	0.10−17.2				0.16	0.15	
Goodwin (1983)	160	97.0−300	0.38−37.4	0.34	0.10	1.21	0.09	0.27	0.36	Townend and Bhatt (1931)	20	298	0.10−60.8				3.21	8.20	
Vapor Pressures																			
Baly and Donnan (1902)	22	69.0−90.0	0.02−0.23	2.73						Michels et al. (1952d)	19	93.3−133	0.32−3.45	0.12					
Clayton and Giauque (1932)	17	69.1−83.1	0.02−0.12	0.37						Parrish and Steward (1975)	6	79.5−120	0.08−1.87	0.59					
Crommelin et al. (1931)	17	68.2−132	0.02−3.44	0.16						Shinoda (1969)	6	68.3−71.5	0.02−0.03	0.60					
Goodwin (1983)	7	90.0−130	0.24−3.04	0.41						Verschoyle (1931)	16	68.2−87.7	0.02−0.19	0.85					
Saturated Liquid Densities																			
Baly and Donnan (1902)	11	71.0−88.0			0.72					Goodwin (1983)	6	95.9−130			0.14				
Barreiros et al. (1982b)	10	80.0−125			0.15					Mathias et al. (1932)	17	73.6−131			0.30	0.64			
Cardoso (1915)	4	123−132			5.84					Terry et al. (1969)	18	77.7−111			0.89				
Saturated Vapor Densities																			
Barreiros et al. (1982b)	10	80.0−125		1.66						Goodwin (1983)	34	70.0−133		0.97		2.17			
Cardoso (1915)	4	123−132		15.8						Mathias et al. (1932)	17	73.6−131		2.32					
Isobaric Heat Capacities																			
Clayton and Giauque (1932)	8	70.0−84.7	0.02−0.14		0.54					Gill and Morrison (1966)	5	68.9−75.8	0.02−0.05		1.55				
Speeds of Sound																			
Van Itterbeek and Mariens (1937)	2	273−292	0.09				0.19												
Enthalpies of Vaporization																			
Clayton and Giauque (1932)	1	81.6		0.39						Gill and Morrison (1966)	1	77.9		0.55					
Second Virial Coefficients																			
Barreiros et al. (1987)	12	100−229		1.71			3.31			Goodwin (1983)	10	120−300		0.08			5.29		
Barreiros et al. (1982b)	10	80.0−125		5.90						McElroy and Buchanan (1995)	7	300−348					8.37		
Brewer (1967)	5	123−223		0.98			2.87			Michels et al. (1952a)	14	273−423					18.0		
Connolly (1964)	5	323−573					3.67			Schmiedel et al. (1980)	12	213−475					22.5		
Elias et al. (1986)	5	77.3-213		6.72			2.27			Vatter et al. (1996)	3	353−463					9.69		
Ideal Gas Isobaric Heat Capacities																			
Hilsenrath et al. (1955)^c	158	70.0−5000		0.01			0.13			Sherratt and Griffiths (1934)^c	5	1273−2073					0.40		
Marsh et al. (1994)^c	139	70.0−5000		0.00			0.02												
Carbonyl Sulfide																			
pρT Data																			
Ihmels and Gmehling (2001)	602	273−623	1.99−40.0		0.05	0.26	1.65	0.70	0.03	Robinson and Senturk (1979b)	75	273−383	0.16−49.7	0.55		0.92	0.90	1.05	0.61
Miranda et al. (1976)	10	266−355	0.53−3.92	3.82	3.02														

Table 9 (Continued)

		temp and pressure ranges		average absolute deviations (AAD/%)^b								temp and pressure ranges		average absolute deviations (AAD/%)^b					
							supercritical fluid										supercritical fluid		
reference	no.	T/K	p/MPa	gas	liq	crit reg	LD	MD	HD	reference	no.	T/K	p/MPa	gas	liq	crit reg	LD	MD	HD
Vapor Pressures																			
Kemp and Giauque (1937)	15	162−224	0−0.11	0.30						Robinson and Senturk (1979a)	13	265−379	0.50−6.33	0.21					
Miranda et al. (1976)	5	266−355	0.53−3.92	4.37															
Saturated Liquid Densities																			
Miranda et al. (1976)	5	266−355			3.29					Pearson et al. (1932)	5	273−305			1.46				
Partington and Neville (1951)	30	174−374			2.05	22.5													
Saturated Vapor Densities																			
Miranda et al. (1976)	5	266−355		6.66															
Isobaric Heat Capacities																			
Kemp and Giauque (1937)	14	137−221	0−0.09		0.97														
Enthalpies of Vaporization																			
Frank and Clusius (1939)	2	214−223		0.20						Kemp and Giauque (1937)	5	223		0.31					
Second Virial Coefficients																			
Bell et al. (1992)	3	290−310		7.54															
Ideal Gas Isobaric Heat Capacities																			
Cross (1935b)^c	16	298−1800		0.06			0.99			McBride and Gordon (1961)^c	41	200−6000		0.00			0.12		
Gordon (1961)^c	59	298−6000		0.02			0.22			Papousek (1959)^c	10	273−1000		0.19			0.37		
Marsh et al. (1994)^c	126	135−5000		0.34			0.18												
Decane																			
pρT Data																			
Audonnet and Padua (2004)	40	303−393	0.10−76.2		0.09					Gouel (1978)	72	293−393	0.10−40.5		0.53				
Banipal et al. (1991)	72	313−373	0.10−10.0		0.03					Reamer et al. (1942)	217	311−511	1.38−68.9		0.54				
Bessieres et al. (2001)	21	308−368	20.0−40.0		0.07					Sagdeev and Mukhamedzyanov (1977)	33	273−373	0.10−98.0		0.30				
Bridgman (1931)	8	273−368	0.10−98.1		0.21					Sage et al. (1940)	55	294−394	1.72−24.1		0.58				
Bridgman (1949)	2	298	49.0−98.1		0.21					Scaife and Lyons (1980)	48	248−373	0.10−98.2		0.18				
Caudwell et al. (2004)	17	298−373	0.10−52.4		0.04					Snyder and Winnick (1970)	55	298−358	0.10−97.5		0.14				
Cullick and Mathis (1984)	4	304−311	6.89−20.6		0.06					Susnar et al. (1992)	51	294	0.10−34.6		0.02				
Dymond et al. (1982)	8	298−373	0.10−89.7		0.10					Takagi and Teranishi (1985a,b)	2	298	0.10−50.0		0.25				
Gates et al. (1986)	18	298−400	0.20−20.5		0.04					Tohidi et al. (2001)	7	323	4.69−93.8		0.66				
Gehrig and Lentz (1983)	259	298−673	0−98.0	4.63	0.74	10.5	2.25		1.76	Zuniga-Moreno et al. (2005)	148	313−363	1.01−25.1		0.01				
Vapor Pressures																			
Allemand et al. (1986)	11	298−348	0	0.65						Linder (1931)	4	269−282	0	11.0					
Batiu (2002)	13	337−377	0−0.01	1.49						Morgan and Kobayashi (1994)	16	323−588	0−1.40	0.11					
Carruth and Kobayashi (1973)	7	244−311	0	15.5						Reamer and Sage (1963)	8	278−511	0−0.45	9.92					
Chirico et al. (1989)	33	268−490	0−0.27	0.05						Reamer et al. (1942)	7	311−511	0−0.45	5.79					
Dejoz et al. (1996)	37	315−458	0−0.13	0.40						Reamer et al. (1946)	7	311−511	0−0.45	5.21					
Edwards and Ibanez (1968)	4	323−398	0−0.02	14.5						Schmelzer and Pusch (1995)	4	363−413	0−0.04	0.05					
Gierycz et al. (1988)	3	373−447	0−0.10	0.09						Viton et al. (1996)	33	244−467	0−0.16	0.56					
Gregorowicz et al. (1987)	15	363−393	0−0.02	0.17						Willingham et al. (1945)	19	368−448	0−0.10	0.02					
Lee et al. (1992)	6	409−584	0.03−1.32	0.99						Willman and Teja (1985)	6	373−394	0−0.02	1.27					
Saturated Liquid Densities																			
Aicart et al. (1981)	4	298−333			0.04					Francis (1957)	24	373−598			0.27				
Aminabhavi et al. (1996)	3	298−308			0.00					Garcia et al. (2002)	5	278−318			0.09				
Aminabhavi and Gopalakrishna (1995)	4	298−313			0.05					Gehrig and Lentz (1983)	3	298−383			0.09				
Aminabhavi and Patil (1997)	3	298−308			0.00					Goates et al. (1979)	3	283−313			0.06				
Aminabhavi and Banerjee (2001)	3	298−308			0.04					Goates et al. (1981)	3	283−313			0.06				
Aminabhavi and Gopalakrishna (1994)	3	298−318			0.04					Inglese et al. (1983)	3	298−318			0.06				

Aminabhavi et al. (1992)	6	298−323			0.04					Mansker et al. (1987)	3	298−338			0.17				
Amirkhanov et al. (1991)	22	274−618			0.61	3.44				Moore and Wellek (1974)	4	293−313			0.05				
Aralaguppi et al. (1999)	3	298−308			0.02					Nayak et al. (2001)	3	298−308			0.40				
Asfour et al. (1990)	4	293−313			0.08					Peleteiro et al. (2002)	5	280−318			0.04				
Beaudoin and Kohn (1967)	7	248−423			0.08					Quayle et al. (1944)	3	293−313			0.07				
Bingham and Fornwalt (1930)	16	273−373			0.20					Reamer et al. (1942)	7	311−511			0.19				
Calvo et al. (1998)	3	288−308			0.06					Reamer et al. (1946)	7	311−511			0.22				
Casas et al. (2002)	3	288−308			0.05					Sage et al. (1940)	5	294−394			0.48				
de Ruiz Holgado et al. (1993)	4	293−308			0.03					Tojo et al. (2004)	4	298−318			0.02				
Diaz Peña and Tardajos (1978)	4	298−333			0.03					Trenzado et al. (2001)	5	283−313			0.02				
Dornte and Smyth (1930)	10	263−443			0.07					Vogel (1946)	4	293−359			0.25				
Dymond and Young (1981)	8	283−393			0.08					Wu et al. (1998)	4	293−313			0.04				
Edwards and Ibanez (1968)	4	323−398			0.75					Yu and Tsai (1995)	5	293−313			0.02				
Saturated Vapor Densities																			
Amirkhanov et al. (1991)	10	578−618		6.09		1.51													
Saturation Liquid Heat Capacities																			
Finke et al. (1954)	17	247−319		1.67						Paramo et al. (2002)	15	278−348		0.58					
Huffman et al. (1931)	6	251−298		0.77						Parks et al. (1930)	5	255−295		0.26					
Osborne and Ginnings (1947)	9	278−318		0.72															
Isobaric Heat Capacities																			
Banipal et al. (1991)	72	318−373	0.10−10.0		0.33					Parks et al. (1930)	5	255−295	0		0.26				
Czarnota (1993)	6	299−299	0.10−86.4		4.01					Peleteiro et al. (2002)	5	280−318	0		0.81				
Gates et al. (1986)	4	298−368	0		0.25					Schlinger and Sage (1952)	13	300−366	0		0.62				
Grigorev et al. (1975)	9	303−462	0.10−0.30		0.69														
Isochoric Heat Capacities																			
Amirkhanov et al. (1991)	34	619−673	2.15−3.76			6.34													
Speeds of Sound																			
Aminabhavi and Gopalakrishna (1994)	3	298−318	0		0.36					Khasanshin and Shchemelev (2001)	40	298−433	0.10−49.1		0.19				
Casas et al. (2002)	3	288−308	0		0.15					Neruchev et al. (1969)	17	293−613	0−1.98		1.38	16.8			
Enthalpies of Vaporization																			
Couch et al. (1963)	10	344−444		0.63						Morawetz (1968)	5	298		1.17					
Ideal Gas Isobaric Heat Capacities																			
Marsh et al. (1994)^c	104	245−5000		0.00			0.03			Scott (1974)^c	15	273−1500		0.03			0.04		
Hydrogen Sulfide																			
pρT Data																			
Ihmels and Gmehling (2001)	468	273−548	2.76−40.0		0.06	2.94	0.67	0.17	0.04	Reamer et al. (1950)	263	278−444	0.10−68.9	1.01	0.43	4.14	0.39	1.07	0.34
Lewis and Fredericks (1968)	94	373−493	9.12−94.6		0.27	13.8		1.87	0.20	Straty (1983)	112	493−523	0.21−37.8				0.49	1.77	
Liu et al. (1986)	106	300−500	1.00−33.0	1.99		2.28	2.44	3.03	3.54	Wright and Maass (1931)	54	238−320	0.03−0.42	0.09					
Rau and Mathia (1982)	67	342−760	6.00−60.0	44.8		15.0	4.71	1.69											
Vapor Pressures																			
Bierlein and Kay (1953)	15	286−370	1.52−8.61	2.15						Klemenc and Bankowski (1932)	7	188−213	0.02−0.11	2.16					
Cardoso (1921)	15	273−370	1.03−8.50	1.29						Lopes and Calado (1996)	22	193−230	0.03−0.22	0.07					
Clark et al. (1951)	5	190−220	0.03−0.14	0.94						Maass and McIntosh (1914)	13	189−215	0.02−0.11	12.3					
Clarke and Glew (1970)	26	195−303	0.04−2.27	0.12						Reamer et al. (1950)	11	283−369	1.38−8.27	1.10					
Fredenslund and Mollerup (1975)	4	203−293	0.06−1.79	0.53						Reamer et al. (1953)	3	278−344	1.17−5.37	0.44					
Giauque and Blue (1936)	9	188−213	0.02−0.10	0.10						Steckel (1945)	3	243−288	0.41−1.61	3.89					
Kay and Brice (1953)	8	283−369	1.38−8.27	0.21						Steele et al. (1906)	33	188−213	0.02−0.10	3.03					
Kay and Rambosek (1953)	20	272−373	1.00−8.94	0.15															
Saturated Liquid Densities																			
Baxter et al. (1934)	7	192−331			1.66					Klemenc and Bankowski (1932)	12	190−212			0.02				
Bierlein and Kay (1953)	15	286−370			0.97	2.02				Reamer et al. (1950)	11	283−369			0.73	1.60			
Clarke and Glew (1970)	16	193−194			0.05					Reamer et al. (1953)	3	278−344			0.59				
Cubitt et al. (1987)	18	197−265			0.23					Steele et al. (1906)	20	190−212			1.62				
Kay and Rambosek (1953)	20	272−373			1.10	3.39													

Table 9 (Continued)

		temp and pressure ranges		average absolute deviations (AAD/%)^b								temp and pressure ranges		average absolute deviations (AAD/%)^b					
							supercritical fluid										supercritical fluid		
reference	no.	T/K	p/MPa	gas	liq	crit reg	LD	MD	HD	reference	no.	T/K	p/MPa	gas	liq	crit reg	LD	MD	HD
Saturated Vapor Densities																			
Bierlein and Kay (1953)	15	286−370		1.34						Reamer et al. (1950)	11	283−369		1.33					
Kay and Rambosek (1953)	13	311−373		0.57		2.79				Reamer et al. (1953)	3	278−344		0.73					
Isobaric Heat Capacities																			
Felsing and Drake (1936)	3	303−383	0.10	5.45			3.72			Millar (1923)	7	216−278	0.12−1.19	13.9					
Giauque and Blue (1936)	6	190−211	0.03−0.09		0.63														
Enthalpies of Vaporization																			
Frank and Clusius (1939)	2	189−213		0.11															
Second Virial Coefficients																			
Khoury and Robinson (1971)	4	323−398		7.93			3.18			Liu (1985)	6	300−500		4.04			14.5		
Lewis and Fredericks (1968)	7	373−493		64.4			10.9												
Ideal Gas Isobaric Heat Capacities																			
Barrow and Pitzer (1949)^c	8	298−1000		0.15			2.78			Felsing and Drake (1936)	3	303−383		4.40			3.18		
Cross (1935a)^c	17	213−1800		0.26			1.47			Marsh et al. (1994)^c	115	190−5000		0.04			1.72		
Evans and Wagman (1952)^c	14	298−1500		0.49			0.19			McBride and Gordon (1961)^c	41	200−6000		0.32			0.17		
2-Methylbutane (Isopentane)																			
pρT Data																			
Bridgman (1931)	8	273−368	0.10−98.1		0.38					Silberberg et al. (1959)	200	323−473	0.10−6.14	0.11		4.05	0.10	0.58	0.11
Houck (1974)	0		>100 MPa							Vohra and Kobe (1959)	117	448−473	2.11−18.4	0.55		3.75	0.07	0.32	0.28
Houck and Heydemann (1971)	0		>100 MPa							Walter et al. (1992)	60	201−260	0.10−90.0		0.28				
Isaac et al. (1954)	108	373−573	0.62−21.6	5.47	1.14	4.61	6.57	4.87	2.05	Young and Thomas (1894)	250	284−423	0−0.12	0.19					
Mopsik (1969)	24	223−298	0.10−81.2		0.05														
Vapor Pressures																			
Aston and Schumann (1942)	27	187−222	0	4.19						Isaac et al. (1954)	3	398−448	1.20−2.80	0.35					
Besserer and Robinson (1975)	4	278−378	0.04−0.79	0.78						Schumann et al. (1942)	13	217−295	0−0.08	0.14					
Ewing and Goodwin (1991)	28	255−323	0.01−0.20	0.08						Silberberg et al. (1959)	6	323−448	0.21−2.79	0.14					
Gallagher et al. (1987)	29	303−455	0.11−3.07	0.21						Silberberg (1958)	12	323−423	0.21−1.87	0.14					
Grummitt et al. (1945)	3	301−302	0.10	1.95						Willingham et al. (1945)	7	289−302	0.07−0.10	0.03					
Hachmuth (1932)	3	273−295	0.04−0.08	0.61						Young (1910)	27	243−460	0−3.30	1.16					
Holcomb et al. (1995)	28	233−407	0−1.40	3.16															
Saturated Liquid Densities																			
Arnold et al. (1965)	37	255−455			0.10					Lesche et al. (1984)	21	115−293			0.09				
Davenport et al. (1966)	20	115−154			0.08					McClune (1976)	13	113−173			0.08				
Gallagher et al. (1987)	9	293−453			0.06					Orrit and Laupretre (1978)	41	125−254			0.04				
Holcomb et al. (1995)	28	233−407			0.16					Seitz et al. (1916)	7	222−273			0.03				
Isaac et al. (1954)	3	398−448			1.85					Timmermans (1912)	58	115−288			0.07				
Landolt and Jahn (1892)	4	287−293			0.13					Young (1910)	24	273−460			0.07	2.26			
Saturated Vapor Densities																			
Arnold et al. (1965)	37	255−455		0.85						Holcomb et al. (1995)	21	311−407		4.94					
Gallagher et al. (1987)	9	293−453		0.90															
Isobaric Heat Capacities																			
Czarnota (1988)	8	289−299	0.10−96.8		3.54					Schumann et al. (1942)	13	120−290	0−0.07		2.19				
Guthrie and Huffman (1943)	83	113−298	0−0.09		2.49					Scott et al. (1951)	10	317−487	0.05−0.10	0.11			0.05		
Parks et al. (1930)	14	121−276	0−0.04		1.71					Van Kasteren and Zeldenrust (1979)	16	120−270	0.10		1.77				
Speeds of Sound																			
Ewing and Goodwin (1992)	67	260−320	0−0.08	0.03						Kling et al. (1953)	13	293−433	0.10−19.6		0.59				
Houck (1974)	0		>100 MPa							Walter et al. (1992)	50	203−243	0.10−90.0		1.82				

Enthalpies of Vaporization																			
Schumann et al. (1942)	4	294−298		1.33						Scott et al. (1951)	3	279−301		0.29					
Enthalpy Differences																			
Van Kasteren and Zeldenrust (1979)	16	120−270	0.10	0.16															
Second Virial Coefficients																			
Das et al. (1977)	10	273−473		3.76			4.12			Silberberg et al. (1959)	8	323−473		5.04			4.10		
Ewing and Goodwin (1992)	7	260−320		1.56						Silberberg et al. (1967)	10	273−473		4.17			0.56		
Scott et al. (1951)	3	279−301		6.36						Zaki et al. (1960)	8	323−473		3.80			2.49		
Ideal Gas Isobaric Heat Capacities																			
Ewing and Goodwin (1992)	7	260−320		0.51						Scott (1974)^c	16	200−1500		0.03			0.14		
Marsh et al. (1994)^c	130	115−5000		0.10			0.48			Scott et al. (1951)^c	19	298−1500		0.07			1.55		
Pitzer and Kilpatrick (1946)^c	14	298−1500		1.40			1.99												
2,2-Dimethylpropane (Neopentane)																			
pρT Data																			
Beattie et al. (1951b)	118	433−434	3.16−3.21			15.9				Gonzalez and Lee (1968)	21	311−444	0.69−55.2		1.58	1.99			1.08
Beattie et al. (1952b)	62	434−548	2.40−32.5	1.01	0.17	2.66	0.64	0.56	0.21	Heichelheim et al. (1962)	256	303−473	0.10−7.41	0.45		4.47	0.37	1.19	2.72
Dawson et al. (1973)	162	343−434	0.57−31.6	0.20	0.11	4.55				Wappmann et al. (1996)	13	314−414	10.0−75.0		0.69				
Vapor Pressures																			
Aston and Messerly (1936)	7	258−283	0.04−0.10	0.10						Hossenlopp and Scott (1981)	8	265−303	0.05−0.20	0.02					
Beattie et al. (1951b)	9	323−434	0.36−3.20	0.07						Leu and Robinson (1988)	5	313−423	0.28−2.81	4.41					
Dawson et al. (1973)	19	343−433	0.59−3.17	0.05						Leu and Robinson (1992)	4	323−413	0.36−2.31	0.51					
Douslin (1970)	8	265−304	0.05−0.20	0.05						McGlashan and McKinnon (1977)	3	373−413	1.12−2.29	0.07					
Enokido et al. (1969)	6	257−261	0.04−0.04	0.52						Osborn and Douslin (1974)	10	268−313	0.06−0.27	0.03					
Heichelheim and McKetta (1963)	6	303−423	0.20−2.70	0.09						Shah et al. (1990)	11	261−424	0.05−2.72	0.90					
Hoepfner et al. (1970)	4	263−293	0.05−0.15	0.05						Stead and Williams (1980)	5	260−300	0.04−0.18	2.16					
Hoepfner et al. (1974)	43	257−293	0.04−0.15	0.10						Whitmore and Fleming (1933)	6	257−283	0.04−0.10	2.28					
Saturated Liquid Densities																			
Benoliel (1941)	8	258−293			0.16					McLure and Barbarin-Castillo (1993)	28	291−432			0.11	0.38			
Dawson et al. (1973)	19	343−433			0.12	1.19				Shinsaka et al. (1985)	12	259−295			0.21				
Hoepfner et al. (1979)	46	257−293			7.36														
Saturated Vapor Densities																			
McLure and Barbarin-Castillo (1993)	25	349−433		1.78		0.58				Dawson et al. (1973)	19	343−433		0.19		0.52			
Isobaric Heat Capacities																			
Aston and Messerly (1936)	4	259−279	0.04−0.09		1.18					Hossenlopp and Scott (1981)	40	298−523	0.06−0.20	0.25			0.05		
Enokido et al. (1969)	3	258−260	0.04−0.04		1.09														
Speeds of Sound																			
Ewing et al. (1986)	164	260−340	0−0.10	0.03						Lainez et al. (1990)	204	263−433	0.48−53.3		0.24				
Ewing et al. (1987)	420	260−323	0−0.11	0.02															
Enthalpies of Vaporization																			
Aston and Messerly (1936)	1	279		0.17						Hossenlopp and Scott (1981)	8	265−303		0.12					
Second Virial Coefficients																			
Ashton and Halberstadt (1958)	14	300−342		9.79						Hossenlopp and Scott (1981)	8	265−303		0.96					
Beattie et al. (1952b)	6	434−548		1.05			1.35			Huff and Reed (1963)	4	303−363		1.15					
Dawson et al. (1973)	9	348−498		0.54			0.70			Kerl and Haeusler (1984)	9	261−366		6.13					
Ewing and Marsh (1979)	6	303−346		3.32						Perez Masia et al. (1964)	5	303−398		3.14					
Ewing et al. (1987)	7	260−323		1.09						Silberberg et al. (1967)	9	303−473		4.55			1.86		
Hamann and Lambert (1954)	13	323−548		1.81			1.26			Strein et al. (1971)	11	296−493		14.8			23.4		
Hamann et al. (1955)	8	303−403		1.32						Zarkova and Hohm (2002)	54	260−790		1.40			21.8		
Heichelheim and McKetta (1963)	9	303−473		9.30			9.00												
Ideal Gas Isobaric Heat Capacities																			
Ewing et al. (1986)	17	260−340		0.91						Marsh et al. (1994)^c	101	260−5000		0.02			0.17		
Ewing et al. (1987)	7	260−323		0.64						Pitzer and Kilpatrick (1946)^c	14	298−1500		0.57			4.80		
Hossenlopp and Scott (1981)	10	298−523		0.15			0.07			Scott (1974)^c	15	273−1500		0.10			0.14		

Table 9 (Continued)

reference	no.	temp and pressure ranges		average absolute deviations (AAD/%)^b						reference	no.	temp and pressure ranges		average absolute deviations (AAD/%)^b					
							supercritical fluid										supercritical fluid		
		T/K	p/MPa	gas	liq	crit reg	LD	MD	HD			T/K	p/MPa	gas	liq	crit reg	LD	MD	HD
2-Methylpentane (Isohexane)																			
pρT Data																			
Bridgman (1931)	8	273−368	0−98.1		0.14					Kelso and Felsing (1940)	74	373−548	0.57−31.6		0.10	0.56	0.27	0.39	0.19
Griskey and Canjar (1964)	7	503−573	2.52−4.09				4.92			Moriyoshi and Aono (1988)	54	298−313	1.80−99.2		0.06				
Vapor Pressures																			
Abara et al. (1988)	4	491−497	2.77−2.98	0.16						Ho and Davison (1979)	4	283−313	0.01−0.05	0.06					
Aucejo et al. (1998)	32	310−360	0.05−0.22	0.21						Holcomb et al. (1995)	30	239−408	0−0.68	3.76					
Chun (1964)	26	348−493	0.16−2.83	0.75						Pokki et al. (2002)	19	301−333	0.03−0.10	0.07					
Funk et al. (1972)	3	283−323	0.01−0.07	0.04						Willingham et al. (1945)	14	286−334	0.02−0.10	0.09					
Saturated Liquid Densities																			
Awwad and Pethrick (1983)	17	233−313			0.13					Holcomb et al. (1995)	30	239−408			0.12				
Davenport et al. (1966)	18	120−154			0.22					Ott et al. (1980)	3	283−313			0.01				
Saturated Vapor Densities																			
Holcomb et al. (1995)	23	307−408		11.1															
Isobaric Heat Capacities																			
Czarnota (1998)	4	298−299	0.10−85.5		0.61					Stull (1937)	21	120−320	0−0.06		4.37				
Douslin and Huffman (1946)	27	121−303	0−0.03		1.60					Waddington et al. (1949)	11	325−471	0.03−0.10	0.10					
Speeds of Sound																			
Awwad and Pethrick (1983)	17	233−313	0−0.05		0.51					Plantier and Daridon (2005)	85	293−373	0.10−90.0		0.41				
Enthalpies of Vaporization																			
Lemons and Felsing (1943)	4	293−353		0.97						Waddington et al. (1949)	4	298−333		0.17					
Second Virial Coefficients																			
Chun et al. (1981)	7	383−497		1.65						Waddington et al. (1949)	4	298−333		3.90					
Ideal Gas Isobaric Heat Capacities																			
Marsh et al. (1994)^c	129	120−5000		0.13			0.86			Scott (1974)^c	16	200−1500		0.04			0.15		
Pitzer and Kilpatrick (1946)^c	9	298−1000		0.99			1.09			Waddington et al. (1949)	5	325−471		0.09					
Krypton																			
pρT Data																			
Barreiros et al. (1982a)	61	129−147	1.04−98.4		0.24					Kimura et al. (1987)	0		>100 MPa						
Beattie et al. (1952a)	175	273−573	2.13−42.1				0.19	0.18		Lahr and Eversole (1962)	0		>100 MPa						
Blagoi and Sorokin (1970)	42	120−170	0.10−50.5		0.26					Novikov et al. (1974)	158	121−298	0.25−50.6	0.15	0.07	0.43	0.13	0.07	0.14
Calado et al. (1986)	35	180−195	3.74−70.1		0.26					Rabinovich et al. (1973)	155	289−738	4.77−41.6				0.21		
Dillard and Robinson (1978)	41	223−323	0.68−14.0			0.07	0.04	0.28		Streett and Staveley (1971)	289	120−220	0.53−95.7		0.07			0.56	0.19
Evers et al. (2002)	22	298−348	0.10−8.54				0.18			Theeuwes and Bearman (1970a)	474	130−240	1.23−29.4	0.35	0.07	1.04		0.13	0.06
Glockler et al. (1933)	10	329−369	2.03−10.1				0.18			Trappeniers et al. (1966)	275	273−423	1.88−99.3				0.03	0.11	0.18
Vapor Pressures																			
Allen and Moore (1931)	26	116−121	0.07−0.11	2.66						Los (1974)	36	116−209	0.07−5.52	3.42					
Beaumont et al. (1961)	9	116−119	0.07−0.09	0.59						Meihuizen and Crommelin (1937)	14	116−209	0.07−5.49	0.56					
Blagoi and Sorokin (1970)	5	120−170	16.4−69.6	97.4						Michels et al. (1952c)	29	116−209	0.07−5.43	0.07					
Bowman et al. (1969)	40	116−209	0.08−5.47	0.23						Peters and Weil (1930)	5	116−122	0.07−0.10	14.6					
Chen et al. (1975a)	71	116−120	0.07−0.11	0.71						Theeuwes and Bearman (1970b)	26	127−208	0.17−5.32	0.09					
Lee et al. (1972)	134	116−130	0.07−0.20	1.09															
Saturated Liquid Densities																			
Mathias et al. (1937)	13	126−208			0.08	0.78				Terry et al. (1969)	24	118−164			0.10				
Streett and Staveley (1971)	9	120−200			0.10					Theeuwes and Bearman (1970b)	21	127−209			0.08	0.27			
Saturated Vapor Densities																			
Mathias et al. (1937)	13	126−208		1.45		3.23				Theeuwes and Bearman (1970b)	4	207−209		0.16		1.35			

										Isobaric Heat Capacities									
Beaumont et al. (1961)	5	117−118	0.08−0.09		0.49														
										Speeds of Sound									
Aziz et al. (1967)	30	117−194	0.08−3.47		0.45					Kimura et al. (1987)	0		>100 MPa						
Baidakov et al. (1985)	210	160−193	0.10−4.01		0.28					Lim and Aziz (1967)	23	116−120	0.07−0.10		0.33				
Blagoi et al. (1967)	17	117−202	0.08−4.38		3.47					Lim et al. (1968)	93	118−205	0.09−6.90		0.25				
Ewing et al. (1985)	26	285−320	0.02−0.11				0.02			Streett et al. (1972)	255	145−240	1.26−69.7	0.95	1.15	1.72	0.40	0.62	0.85
										Enthalpies of Vaporization									
Beaumont et al. (1961)	1	117		0.71															
										Second Virial Coefficients									
Brewer (1967)	5	123−223		1.42			1.98			Schmiedel et al. (1980)	12	213−475					2.03		
Byrne et al. (1968)	12	117−252		0.95			2.32			Schramm et al. (1977)	12	202−497		3.40			2.14		
Dillard and Robinson (1978)	3	223−323					0.15			Streett and Staveley (1971)	9	120−200		1.39					
Fender and Halsey (1962)	6	119−138		0.72						Thomaes and van Steenwinkel (1962)	8	134−270		2.70			4.85		
Patel et al. (1988)	3	223−323					1.22			Trappeniers et al. (1966)	7	273−423					18.8		
Perez et al. (1980)	5	300−500					3.25			Weir et al. (1967)	10	118−224		1.36			3.38		
Rentschler and Schramm (1977)	6	300−715					25.6			Whalley and Schneider (1954)	9	273−873					9.21		
Santafe et al. (1976)	6	273−323					0.68												
										Nitrous Oxide									
										pρT Data									
Britton (1929)	27	293−340	1.22−5.02	9.98			4.21			Ihmels (2004)	364	273−523	9.98−40.0		0.04	2.07	0.20	0.15	0.07
Cabanas et al. (1998)	8	308−318	7.64−15.0		2.06	11.0	0.54		1.36	Langenfeld et al. (1992)	11	313−423	8.21−51.8				0.40	5.37	2.36
Castells et al. (1994)	7	308−323	7.64−15.0		0.35	5.10	0.82	0.06	0.05	Ohgaki et al. (1990)	90	308−311	7.02−8.04	2.17	0.12	2.86		1.10	
Couch et al. (1961)	534	243−423	0.10−31.9	0.68	0.25	6.91	0.16	0.23	0.16	Schamp et al. (1962)	113	273−423	1.62−16.8	0.01		0.68	0.03	0.23	
Hirth (1958)	256	243−423	0.10−6.43	0.05			0.06			Yokoyama et al. (1994)	373	310−318	0.10−9.55			5.11	0.38	0.42	
Hurly (2004)	151	225−375	0.11−3.30	1.25			0.29												
										Vapor Pressures									
Blue and Giauque (1935)	4	183−186	0.09−0.11	0.30						Hunter (1906)	9	182−187	0.07−0.11	10.8					
Burrell and Robertson (1915)	4	183−184	0.09−0.10	1.09						Kuenen (1895)	5	278−305	3.57−6.63	1.73					
Cook (1953)	16	286−307	4.27−6.86	0.18						Machado et al. (1980)	1	182	0.09	0.02					
Couch et al. (1961)	18	243−309	1.32−7.23	0.15						Ohgaki et al. (1990)	7	308−309	7.04−7.21	0.09					
Fonseca and Lobo (1989)	1	182	0.09	0.04						Parrish and Steward (1975)	7	195−285	0.18−4.22	0.95					
Hirth (1958)	15	243−303	1.31−6.32	0.17						Zeininger (1972)	6	213−293	0.39−5.01	4.97					
Hoge (1945)	31	183−237	0.09−1.07	0.20															
										Saturated Liquid Densities									
Cook (1953)	14	293−307			0.39	0.29				Machado et al. (1980)	1	182			0.23				
Couch et al. (1961)	12	243−309			0.48	0.97				Ohgaki et al. (1990)	7	308−309				0.76			
Kuenen (1895)	4	278−309			2.46	28.0				Quinn and Wernimont (1929)	17	223−303			1.48				
Leadbetter et al. (1964)	17	182−185			0.34														
										Saturated Vapor Densities									
Cook (1953)	12	293−307		0.75						Ohgaki et al. (1990)	3	309−309				1.49			
Couch et al. (1961)	12	243−309		0.44		1.64				Quinn and Wernimont (1929)	17	223−303		15.6					
Kuenen (1895)	6	278−309		2.06		12.3													
										Saturation Liquid Heat Capacities									
Haase and Tillmann (1994)	20	295−309		4.89															
										Isobaric Heat Capacities									
Blue and Giauque (1935)	5	184−187	0.09−0.12		2.58														
										Isochoric Heat Capacities									
Haase and Tillmann (1994)	9	310−319	7.30−8.76			18.9													
										Speeds of Sound									
Hurly (2003)	312	220−460	0.10−1.64	0.03			0.04			Hurly (2004)	152	225−375	0.11−3.30	0.11			0.05		

Table 9 (Continued)

reference	no.	temp and pressure ranges		average absolute deviations (AAD/%)^b						reference	no.	temp and pressure ranges		average absolute deviations (AAD/%)^b					
							supercritical fluid										supercritical fluid		
		T/K	p/MPa	gas	liq	crit reg	LD	MD	HD			T/K	p/MPa	gas	liq	crit reg	LD	MD	HD
Enthalpies of Vaporization																			
Couch et al. (1961)	18	243−309		2.27						Mills (1909)	5	248−303		7.13					
Hoge (1945)	12	184−205		0.54															
Second Virial Coefficients																			
Couch et al. (1961)	10	243−423		1.67			1.66			Kirouac and Bose (1973)	6	280−348		3.34			4.02		
Elias et al. (1986)	5	187−296		2.88						Schamp et al. (1962)	7	273−423		0.17			0.36		
Hurly (2003)	39	200−1000		0.32			8.50			Turlington and McKetta (1961)	7	243−348		1.17			12.1		
Johnston and Weimer (1934)	46	197−298		11.7															
Ideal Gas Isobaric Heat Capacities																			
Hurly (2003)	13	220−460		0.03			0.03			McBride and Gordon (1961)^c	41	200−6000		0.11			0.79		
Kassel (1934)^c	27	250−1500		0.30			1.34			Pennington and Kobe (1954)^c	15	273−1500		0.11			0.10		
Nonane																			
pρT Data																			
Banipal et al. (1991)	72	313−373	0.10−10.0		0.07					Doolittle (1964)	35	303−573	5.00−50.0		0.27				
Boelhouwer (1960)	44	303−393	0.10−98.1		0.22					Grindley and Lind (1978)	52	303−423	20.0−80.0		0.02				
Carmichael et al. (1953)	86	311−511	0.17−69.2		0.30					Scaife and Lyons (1980)	126	248−373	0.10−98.2		0.12				
Vapor Pressures																			
Berro and Weclawski (1986)	4	333−363	0−0.01	0.07						Paul et al. (1986)	6	333−424	0−0.10	0.32					
Carmichael et al. (1953)	13	311−511	0−0.66	0.57						Stadnicki (1962)	4	401−424	0.05−0.10	0.85					
Carruth and Kobayashi (1973)	9	224−308	0	18.3						White and Rose (1931)	3	424−424	0.10	0.15					
Forziati et al. (1949)	20	343−425	0−0.10	0.04						Willingham et al. (1945)	20	343−425	0−0.10	0.05					
Krafft (1882)	6	313−423	0−0.10	6.22						Wolff et al. (1964)	3	253−293	0	18.4					
Ortega et al. (2001)	46	403−439	0.06−0.15	0.96															
Saturated Liquid Densities																			
Aicart et al. (1980)	4	298−333			0.04					Dornte and Smyth (1930)	11	223−423			0.05				
Aminabhavi et al. (1996)	3	298−308			0.00					Forziati and Rossini (1949)	3	293−303			0.03				
Aminabhavi and Gopalakrishna (1995)	4	298−313			0.09					Garcia et al. (1988)	5	288−308			0.00				
Aminabhavi and Patil (1997)	3	298−308			0.01					Garcia et al. (1991)	6	288−318			0.04				
Aminabhavi and Banerjee (2001)	3	298−308			0.09					Goates et al. (1979)	3	283−313			0.03				
Aminabhavi and Gopalakrishna (1994)	3	298−318			0.10					Goates et al. (1981)	3	283−313			0.04				
Aminabhavi et al. (1992)	6	298−323			0.12					Grindley and Lind (1978)	13	303−423			0.10				
Amirkhanov et al. (1991)	27	273−595			0.37	2.65				Moore and Wellek (1974)	4	293−313			0.03				
Aralaguppi et al. (1999)	3	298−308			0.12					Nayak et al. (2001)	3	298−308			0.02				
Bingham and Fornwalt (1930)	8	273−373			0.22					Pereira et al. (2002)	4	288−308			0.02				
Boelhouwer (1960)	4	303−393			0.03					Plebanski et al. (1986)	10	300−390			0.05				
Calvo et al. (1998)	3	288−308			0.01					Quayle et al. (1944)	3	293−313			0.05				
Carmichael et al. (1953)	13	311−511			0.22					Rodriguez et al. (1999)	3	288−298			0.02				
Casas et al. (2002)	3	288−308			0.04					Tojo et al. (2004)	5	293−318			0.01				
Diaz Peña and Tardajos (1978)	4	298−333			0.03					Tovar et al. (1997)	4	278−308			0.02				
Dixon (1959)	3	293−333			0.03					Vogel (1946)	4	293−359			0.14				
Doolittle and Peterson (1951)	5	263−423			0.07					Wagner and Heintz (1986)	3	293−333			0.02				
Doolittle (1964)	6	303−523			1.07					Yu and Tsai (1995)	5	293−313			0.02				
Saturated Vapor Densities																			
Amirkhanov et al. (1991)	10	553−594		3.49		1.29													
Saturation Liquid Heat Capacities																			
Finke et al. (1954)	22	225−314		1.14						Osborne and Ginnings (1947)	9	278−318		0.35					
Huffman et al. (1931)	8	228−298		0.82															

Isobaric Heat Capacities																			
Banipal et al. (1991)	72	318−373	0.10−10.0		0.47					Tovar et al. (1997)	3	288−308	0		0.44				
Parks et al. (1930)	8	225−299	0		0.71														
Isochoric Heat Capacities																			
Amirkhanov et al. (1991)	226	425−693	0−19.8	1.51	1.09	7.62	0.37	0.91	2.58										
Speeds of Sound																			
Aminabhavi and Gopalakrishna (1994)	3	298−318	0		0.17					Kling et al. (1953)	24	293−373	0.10−49.0		0.36				
Boelhouwer (1967)	59	253−413	0−90.0		0.39					Lago et al. (2005)	61	293−393	0.11−99.9		0.29				
Casas et al. (2002)	3	288−308	0		0.16					Pereira et al. (2002)	4	288−308	0		0.11				
Golik and Ivanova (1962)	6	293−343	0		0.28					Rodriguez et al. (1999)	3	288−298	0		0.16				
Enthalpies of Vaporization																			
Majer et al. (1984)	4	328−368		0.16						Osborne and Ginnings (1947)	1	298		0.15					
Ideal Gas Isobaric Heat Capacities																			
Marsh et al. (1994)[c]	109	220−5000		0.00			0.06			Scott (1974)[c]	15	273−1500		0.04			0.05		
Sulfur Dioxide																			
pρT Data																			
Hellwig (1955)	648	323−518	0.57−31.6	0.88	0.78	6.90	0.70	1.26	1.07	Kang (1960)	510	323−523	0.57−31.6	0.24	0.36	4.30	0.16	0.71	0.37
Hirth (1958)	234	283−473	0.10−6.88	0.12			0.07			Kang et al. (1961)	224	323−431	0.86−31.8		0.35	16.2			
Ihmels et al. (2003)	363	273−523	0.92−35.0		0.02	0.23	0.58	0.17	0.03										
Vapor Pressures																			
Ayscough et al. (1965)	14	253−283	0.06−0.23	0.36						Kang (1960)	23	323−430	0.86−7.88	0.50					
Brady and O’Donnell (1968)	7	289−313	0.29−0.63	0.17						Lorimer et al. (1975)	15	228−250	0.02−0.05	0.77					
Burrell and Robertson (1915)	14	200−262	0−0.10	5.13						Noles and Zollweg (1991)	6	283−425	0.23−7.19	0.59					
Gardner and Day (1984)	6	273−298	0.16−0.39	0.31						Riedel (1939)	21	213−303	0−0.46	0.08					
Giauque and Stephenson (1938)	13	201−263	0−0.10	0.74						Stock (1923)	51	220−270	0−0.14	0.11					
Hellwig (1955)	10	323−431	0.86−7.88	0.71						Toriumi and Hara (1944)	14	296−428	0.36−7.44	0.65					
Hirth (1958)	34	273−423	0.15−6.97	0.20															
Saturated Liquid Densities																			
Cailletet and Mathias (1887)	14	273−428			0.69	7.77				Kang (1960)	23	323−430			0.61	4.56			
Cardoso and Sorrentino (1927)	12	287−430			0.36	1.22				Seyer and Peck (1930)	16	223−373			0.23				
Saturated Vapor Densities																			
Cailletet and Mathias (1887)	15	280−428		4.78		11.9				Kang (1960)	23	323−430		1.70		6.11			
Cardoso and Sorrentino (1927)	12	287−430		14.0		3.86													
Isobaric Heat Capacities																			
Bass and Lamb (1957)	3	273−323	0.16−0.84		2.67					Perlick (1937a)	23	202−291	0−0.31		1.74				
Giauque and Stephenson (1938)	12	202−261	0−0.09		0.33					Riedel (1939)	10	234−273	0.02−0.16		0.20				
Enthalpies of Vaporization																			
Mills (1909)	11	263−428		6.01						Riedel (1939)	5	254−288		0.24					
Second Virial Coefficients																			
Kang et al. (1961)	11	283−473		3.54			1.26			Stryjek and Kreglewski (1965)	4	298−368		5.68					
Riedel (1939)	13	278−323		1.11															
Ideal Gas Isobaric Heat Capacities																			
Barrow and Pitzer (1949)[c]	8	298−1000		0.13			0.68			Kobe and Long (1950)[c]	23	273−3000		0.07			1.36		
Cross (1935b)[c]	16	298−1800		0.28			1.15			Marsh et al. (1994)[c]	113	200−5000		0.47			2.05		
Evans and Wagman (1952)[c]	14	298−1500		0.03			0.09			McBride and Gordon (1961)[c]	41	200−6000		0.02			0.06		
Gordon (1961)[c]	59	298−6000		0.03			0.07			Nagarajan (1963)[c]	18	200−1700		0.16			1.11		
Toluene																			
pρT Data																			
Akhundov and Abdullaev (1970)	303	298−673	0.27−50.4	0.48	0.08	1.00	1.06	1.37	0.16	Magee and Bruno (1996)	311	180−400	0.52−35.1		0.04				
Akhundov and Abdullaev (1971)	482	573−673	0.38−50.5	1.31	0.11	1.14	1.18	1.27	0.20	Marcos et al. (1983)	92	423−498	0.09−0.85	0.22					
Akhundov et al. (1973)	71	592−603	3.69−5.05			1.98	2.52	0.92	0.24	Masui (2002)	65	298−423	0.04−30.2		0.03				
Albert et al. (1985)	19	298−400	0.20−20.5		0.02					McGregor (1989)	54	350−600	0.84−14.0		0.19				0.19

Table 9 (Continued)

		temp and pressure ranges		average absolute deviations (AAD/%)^b								temp and pressure ranges		average absolute deviations (AAD/%)^b					
							supercritical fluid										supercritical fluid		
reference	no.	*T*/K	*p*/MPa	gas	liq	crit reg	LD	MD	HD	reference	no.	*T*/K	*p*/MPa	gas	liq	crit reg	LD	MD	HD
Toluene (continued)																			
pρT Data																			
Avelino et al. (2003)	80	223−348	0.10−80.6		0.06					Mopsik (1969)	24	223−298	0.10−81.2		0.06				
Bazaev et al. (2001)	159	591−673	4.02−35.5	15.4	1.12	9.29	9.81	4.07	0.84	Opel et al. (1974)	32	393−584	0.06−0.19	0.04					
Belonenko et al. (2000)	11	323−323	0.10−93.6		0.05					Poehler and Kiran (1996)	69	323−423	3.42−64.8		0.21				
Dymond et al. (1988)	38	298−373	0.10−99.4		0.04					Skinner et al. (1968)	0		>100 MPa						
Dymond et al. (1991)	16	298−373	0.10−76.3		0.05					Siddiqi and Teja (1988)	24	298−338	0.10−34.5		0.62				
Easteal and Woolf (1985)	19	278−323	3.03−91.3		0.83					Sousa et al. (1992b)	56	300−403	0.66−26.1		0.03				
Et-Tahir et al. (1995)	45	298−363	0.10−40.0		0.21					Straty et al. (1988)	320	348−723	0.21−36.2	2.07	0.19	6.28	1.00	1.46	0.19
Franck et al. (1998)	45	323−673	5.00−75.0		0.44				0.85	Takagi and Teranishi (1984)	15	293−303	0.10−80.0		0.18				
Gouel (1978)	90	294−393	5.17−40.6		0.35					Taravillo et al. (1994)	46	223−303	0.13−99.3		0.14				
Gupta and Hanks (1977)	24	273−363	2.76−22.1		0.34					Verveiko et al. (1991)	16	323−423	0.10−50.0		0.08				
Ihmels and Gmehling (2001)	497	273−623	0.47−30.0		0.04	0.65		0.23	0.09	Watanabe et al. (1988)	22	503−603	1.08−3.53	3.60			1.25		
Kashiwagi et al. (1982)	37	273−373	0.10−99.9		0.04					Watson (2000)	95	273−353	0.10−30.1		0.01				
Kashiwagi and Makita (1982)	75	298−348	0.10−97.3		0.04					Weber (2004)	64	286−371	0.11−30.5		0.00				
Vapor Pressures																			
Akhundov and Abdullaev (1969)	38	423−591	0.28−4.09	0.10						Martinez-Soria et al. (1999)	16	348−393	0.03−0.13	0.10					
Akhundov and Abdullaev (1977)	35	298−583	0−3.71	0.08						Michou-Saucet et al. (1990)	10	298−343	0−0.03	0.52					
Ambrose (1987)	47	398−592	0.15−4.10	0.16						Milazzo (1956)	10	210−293	0	4.84					
Ambrose et al. (1967)	9	420−580	0.26−3.56	0.09						Mokbel et al. (1998)	24	199−402	0−0.17	1.07					
Ashcroft et al. (1979)	6	298−313	0	0.73						Munday et al. (1980)	7	273−322	0−0.01	0.32					
Barker (1910)	6	195−299	0	5.93						Muthu et al. (1980)	3	293−393	0−0.13	0.68					
Besley and Bottomley (1974)	34	273−298	0	0.22						Myers et al. (1979)	10	349−384	0.03−0.10	0.68					
Chirico and Steele (1994)	21	305−422	0−0.27	0.01						Natarajan and Viswanath (1985)	16	380−521	0.10−1.68	4.44					
Dreyer et al. (1955)	8	313−383	0−0.10	0.22						Pitzer and Scott (1943)	5	273−323	0−0.01	0.26					
Forziati et al. (1949)	19	309−385	0−0.10	0.03						Reddy and Rao (1965)	4	353−384	0.04−0.10	0.24					
Francesconi et al. (1982)	5	335−382	0.02−0.10	1.09						Reich et al. (1998)	19	320−384	0.01−0.10	0.16					
Funk et al. (1972)	3	283−323	0−0.01	0.13						Rogalski (1985)	3	373	0.07−0.07	0.09					
Gaw and Swinton (1968)	5	303−343	0−0.03	0.02						Schmoll and Jenckel (1956)	8	293−328	0−0.02	0.60					
Guzman et al. (1981)	5	333−358	0.02−0.05	0.33						Schneider (1960)	5	333−373	0.02−0.07	0.04					
Kassmann and Knapp (1986)	4	313−384	0−0.10	0.13						Scott (1986)	11	302−368	0−0.06	0.15					
Katayama and Watanabe (1980)	5	330−384	0.02−0.10	0.44						Steinhagen and Sandler (1994)	3	293−333	0−0.02	0.41					
Klara et al. (1987)	6	325−500	0.01−1.18	0.57						Tan and Ti (1988)	5	318−383	0.01−0.10	3.41					
Kokkonen and Arvola (1984)	5	293−333	0−0.02	0.70						Vera and Prausnitz (1971)	3	283−323	0−0.01	0.24					
Krase and Goodman (1930)	20	305−575	0−3.28	3.36						VonNiederhausern et al. (2000)	40	586−592	3.90−4.14	0.52					
Kuus et al. (2003)	4	343−384	0.03−0.10	0.09						Watanabe et al. (1988)	10	504−587	1.25−3.89	0.17					
Lee and Holder (1993)	13	331−496	0.02−1.10	0.61						Weber (1955)	3	342−384	0.03−0.10	0.38					
Li et al. (1972)	7	295−314	0	2.53						Willingham et al. (1945)	20	308−385	0−0.10	0.04					
Linder (1931)	8	263−270	0	1.69						Willman and Teja (1985)	7	373−394	0.08−0.13	0.27					
Macedo et al. (1984)	14	318−350	0−0.03	0.08						Zmaczynski (1930)	13	353−429	0.04−0.31	0.08					
Saturated Liquid Densities																			
Akhundov and Abdullaev (1977)	35	298−583			0.15					Lopez et al. (2000)	6	278−323			0.00				
Asfour et al. (1990)	4	293−313			0.05					Magee and Bruno (1996)	19	180−359			0.04				
Bean (1999)	3	288−298			0.00					Mamedov and Panchenkov (1955)	11	253−353			0.19				
Chirico and Steele (1994)	8	303−590			0.36	3.35				Mason and Paxton (1939)	4	252−323			0.01				
Cowley and Partington (1936)	5	195−293			0.13					Massart (1936)	14	178−400			0.03				
Deshpande and Bhatgadde (1968)	3	298−318			0.01					Moumouzias and Ritzoulis (1992)	5	288−308			0.02				
Deshpande and Bhatgadde (1971)	3	298−318			0.01					Nikam et al. (2000)	3	303−313			0.12				
Dymond and Robertson (1985)	7	288−393			0.07					Palaiologou and Molinou (1995)	5	283−303			0.01				
Exarchos et al. (1995)	5	293−313			0.02					Polikhronidi et al. (2001)	3	562−588			4.15				
Forziati and Rossini (1949)	3	293−303			0.02					Prengle et al. (1967)	7	301−363			0.01				
Francesconi and Comelli (1991)	9	289−307			0.01					Rabe (1981)	42	185−301			0.34				

Francis (1957)	25	343−578			0.31					Rattan et al. (2002)	4	293−323			0.05				
Garbajosa et al. (1982)	4	298−333			0.02					Rozhnov (1967)	4	303−413			0.05				
George and Sastry (2003)	4	298−313			0.00					Shraiber and Pechenyuk (1965)	8	293−363			0.05				
Gross (1993)	11	213−313			0.06					Singh and Sinha (1985)	5	298−333			1.07				
Hafez and Hartland (1976)	4	293−318			0.01					Singh et al. (1989)	5	298−333			1.07				
Hales and Townsend (1972)	14	293−490			0.00					Singh et al. (1990)	5	298−333			1.07				
Hammond et al. (1958)	9	293−384			0.03					Steele et al. (1989)	6	303−428			0.07				
Heine and Snyder (1984)	5	283−323			0.02					Swain et al. (1999)	5	298−318			0.23				
Kahl et al. (2003)	12	278−333			0.04					Tamura et al. (1985)	3	293−303			0.00				
Katz et al. (1971)	4	298−313			0.01					Vogel (1948)	9	292−360			0.18				
Saturated Vapor Densities																			
Akhundov and Abdullaev (1977)	35	298−583		0.38						Polikhronidi et al. (2001)	2	590−592		11.1		24.5			
Chirico and Steele (1994)	2	587−589		16.7															
Saturation Liquid Heat Capacities																			
Becker and Gmehling (2001)	13	310−370		0.15						Paramo et al. (2002)	15	278−348		0.15					
Becker et al. (2000)	22	288−353		0.24						Paramo et al. (2003)	13	288−348		0.26					
Chirico and Steele (1994)	15	300−570		0.64						Steele et al. (1989)	29	300−580		1.50					
Isobaric Heat Capacities																			
Akhundov and Eksaev (1973a)	104	554−673	2.50−25.0	5.73	1.04	2.71	0.61	2.94	1.69	Pitzer and Scott (1943)	3	393−463	0.05−0.10	0.55					
Akhundov and Eksaev (1973b)	189	303−634	0.50−25.0		0.92	28.2				Rastorguev et al. (1975)	9	303−463	0.10−0.72		0.34				
Akhundov et al. (1973)	828	298−673	0−20.0	1.42	0.43	2.61	0.49	1.90	1.84	Rastorguev and Ganiev (1967)	5	293−373	0−0.07		0.96				
Andolenko and Grigorev (1979)	9	293−373	0−0.07		0.42					Sampaio and Nieto de Castro (1998)	14	308−373	0−0.07		0.41				
Deshpande and Bhatgadde (1971)	3	298−318	0		0.74					San Jose et al. (1976)	38	393−503	0.13−2.50		1.72				
Eubank et al. (1984)	8	353−493	2.00		4.81					Scott et al. (1962)	38	183−500	0−0.20	0.48	0.40				
Hwa and Ziegler (1966)	34	181−304	0		0.49					Shulga et al. (1986)	20	256−401	3.50−91.8		0.70				
Jadot and Fraiha (1989)	10	315−405	0−0.18		0.59					Smith and Andrews (1931)	9	184−298	0		1.44				
Nefedov and Filippov (1980)	80	300−620	0−30.0		1.01			18.1	2.59	Stephens and Olson (1984)	11	266−318	0		1.10				
Okhotin et al. (1987)	15	181−380	0−0.09		0.89					Williams and Daniels (1925)	5	293−333	0−0.02		2.89				
Pedersen et al. (1975)	19	301−347	0−0.03		0.44														
Isochoric Heat Capacities																			
Polikhronidi et al. (2001)	136	562−620	2.85−7.09	35.6	20.2	32.9		19.5											
Speeds of Sound																			
Deshpande and Bhatgadde (1968)	3	298−318	0		0.43					Pankevich and Zotov (1976)	85	473−633	0.73−32.7		0.74			4.22	0.87
Deshpande and Bhatgadde (1971)	3	298−318	0		0.43					Takagi and Teranishi (1984)	15	293−303	0.10−80.0		0.19				
Freyer et al. (1929)	6	273−323	0−0.01		0.20					Takagi and Teranishi (1985a,b)	10	303	0.10−90.0		0.38				
Heine and Snyder (1984)	5	283−323	0−0.01		0.23					Tamura et al. (1985)	3	293−303	0		0.19				
Muringer et al. (1985)	38	179−320	0.10−81.1		0.33					Verveiko et al. (1991)	12	293−373	0.10−50.0		0.27				
Nath and Tripathi (1983)	3	298−308	0		0.27					Will et al. (1998)	57	323−591	0.01−4.10	2.80	2.23	4.48			
Okhotin et al. (1988)	248	183−523	0.10−58.9		0.27					Zotov et al. (1969)	28	293−573	0−3.28	1.96	0.80				
Enthalpies of Vaporization																			
Andon et al. (1957)	2	298−384		0.16						Natarajan and Viswanath (1985)	16	380−521		0.36					
Eubank et al. (1984)	9	333−493		1.38						Scott et al. (1962)	4	341−410		0.11					
Enthalpy Differences																			
Eubank et al. (1984)	44	333−513	0.12−9.41	0.71															
Second Virial Coefficients																			
Andon et al. (1957)	4	349−393		3.76						Marcos et al. (1983)	4	423−498		1.29					
Cox and Andon (1958)	3	409−438		2.28						Opel et al. (1974)	10	413−583		2.41					
Kolysko et al. (1973)	10	373−493		3.94						Scott et al. (1962)	4	341−410		3.37					
Ideal Gas Isobaric Heat Capacities																			
Chao et al. (1984)^c	22	200−3000		1.17			1.56			Pitzer and Scott (1943)^c	10	298−1500		0.31			0.47		
Marsh et al. (1994)^c	117	180−5000		0.00			0.24			Scott et al. (1962)^c	20	273−1500		0.30			1.39		

Table 9 (Continued)

reference	no.	temp and pressure ranges		average absolute deviations (AAD/%)^b						reference	no.	temp and pressure ranges		average absolute deviations (AAD/%)^b					
							supercritical fluid										supercritical fluid		
		T/K	p/MPa	gas	liq	crit reg	LD	MD	HD			T/K	p/MPa	gas	liq	crit reg	LD	MD	HD
Xenon																			
pρT Data																			
Baidakov et al. (1992)	212	265−290	3.52−6.06	0.48	0.21	1.41	1.05	1.08		Lahr and Eversole (1962)	0		>100 MPa						
Beattie et al. (1951a)	178	290−573	2.09−41.2			9.14	0.34	0.68		Michels et al. (1954)	388	273−423	1.67−99.4	0.07		0.20	0.07	0.12	0.15
Blagoi and Sorokin (1970)	34	172−220	0.15−50.5		0.21					Rabinovich et al. (1973)	175	292−740	4.45−45.0			2.78	0.17	0.40	
Calado et al. (1986)	16	180−195	6.08−69.5		0.48					Streett et al. (1973)	403	165−290	0.41−97.0		0.25			0.49	0.36
Duarte et al. (2000)	56	273−287	2.88−6.45	1.01	0.24					Theeuwes and Bearman (1970c)	274	167−240	0.58−29.4		0.11				
Habgood and Schneider (1954)	228	289−292	5.74−6.11			3.65				Ulybin et al. (1974)	77	162−298	0.19−53.4	0.13	0.06	0.55	0.11	0.20	0.00
Hurly et al. (1997)	45	273−358	0.29−3.35	0.04			0.03												
Vapor Pressures																			
Allen and Moore (1931)	13	161−169	0.08−0.11	4.96						Habgood and Schneider (1954)	4	286−289	5.41−5.77	0.02					
Baidakov et al. (1992)	16	265−290	3.47−5.83	0.04						Heuse and Otto (1932)	19	162−166	0.08−0.11	0.42					
Blagoi and Sorokin (1970)	4	172−220	0.15−1.05	1.11						Michels and Wassenaar (1950)	38	162−289	0.08−5.77	0.04					
Bowman et al. (1969)	35	162−289	0.08−5.74	0.11						Nunes da Ponte et al. (1985)	8	210−284	0.75−5.23	0.15					
Chen et al. (1975a)	29	161−165	0.08−0.10	0.15						Patterson et al. (1912)	4	253−283	2.54−5.16	1.70					
Clusius and Weigand (1939)	10	189−273	0.32−4.14	2.09						Theeuwes and Bearman (1970d)	30	175−289	0.17−5.81	0.12					
Fonseca and Lobo (1989)	3	161−195	0.08−0.44	0.18															
Saturated Liquid Densities																			
Baidakov et al. (1992)	16	265−290			0.21	1.38				Terry et al. (1969)	15	164−219			0.09				
Duarte et al. (2000)	5	273−287			0.16	0.64				Theeuwes and Bearman (1970d)	21	166−236			0.22				
Leadbetter and Thomas (1965)	21	162−273			0.42					Weinberger and Schneider (1952)	23	288−290				2.38			
Patterson et al. (1912)	15	206−289			4.28	7.62				Whiteway and Mason (1953)	20	290−290				2.47			
Streett et al. (1973)	6	170−240			0.15														
Saturated Vapor Densities																			
Baidakov et al. (1992)	5	287−290		0.38		2.42				Weinberger and Schneider (1952)	21	289−290				2.81			
Duarte et al. (2000)	5	273−287		0.98						Whiteway and Mason (1953)	20	290−290				1.96			
Patterson et al. (1912)	15	206−289		2.22		4.94													
Isobaric Heat Capacities																			
Clusius and Riccoboni (1938)	7	163−166	0.09−0.11		0.39														
Isochoric Heat Capacities																			
Kline and Carome (1973)	41	290−298	5.85−6.83			40.5													
Speeds of Sound																			
Aziz et al. (1967)	60	162−272	0.08−4.05		0.41					Hurly et al. (1997)	232	210−400	0.04−1.45	0.12			0.02		
Baidakov et al. (1985)	169	220−270	0.10−4.00		0.36					Kline and Carome (1973)	49	290−298	5.84−6.83			34.8			
Blagoi et al. (1967)	23	162−270	0.09−4.12		0.97					Lim et al. (1968)	116	165−285	0.69−6.60		0.29				
Gillis et al. (2004)	85	290−300	5.85−7.09			12.1				Pitaevskaya et al. (1975)	24	298−473	40.0−80.0					2.97	2.24
Second Virial Coefficients																			
Hahn et al. (1974)	11	201−650		0.91			2.03			Schmiedel et al. (1980)	12	213−475		2.08			1.19		
Hohm and Truemper (1995)	7	294−1080					29.9			Schramm and Mueller (1982)	8	213−450		4.81			5.57		
Michels et al. (1954)	9	273−423		1.75			21.3			Schramm et al. (1977)	11	231−491		1.47			1.91		
Reeves and Whytlaw-Gray (1955)	5	273−313		3.16			3.56			Streett et al. (1973)	12	165−270		0.93					
Rentschler and Schramm (1977)	7	309−713					4.11			Whalley et al. (1955)	9	273−974		3.63			7.05		
Hexafluoroethane (R-116)																			
pρT Data																			
Kijima et al. (1977)	116	209−367	0.19−8.23	0.29		5.61	0.17	2.42		Pace and Aston (1948)	7	298	0.05−0.10				0.04		
Maslennikov (1994)	79	183−315	0.96−55.0		0.13	4.02	2.39		0.40										

										Vapor Pressures							
Kao and Miller (2000)	55	177−291	0.03−2.90	0.14						Pace and Aston (1948)	8	180−195	0.04−0.10	0.85			
Kijima et al. (1977)	83	188−293	0.07−3.01	0.31						Ruff and Bretschneider (1933)	8	174−196	0.03−0.11	1.56			
Kim (1974)	7	269−292	1.70−3.01	0.65													
										Saturated Liquid Densities							
Gunchuk et al. (1989)	20	175−270			0.03					Saikawa et al. (1979)	12	291−293				1.52	
Pace and Aston (1948)	8	180−195			0.20					Swarts (1933)	8	195−292			0.71	3.01	
										Saturated Vapor Densities							
Pace and Aston (1948)	8	180−195		0.71						Swarts (1933)	8	195−292		11.7		0.40	
Saikawa et al. (1979)	14	291−293		0.96		0.93											
										Isobaric Heat Capacities							
Hejmadi et al. (1977)	10	292−293	3.01−3.01			13.6				Pace and Aston (1948)	10	175−191	0.03−0.08		0.20		
Kim (1974)	115	255−394	1.70−13.6	9.38	8.79	7.08	5.82	6.05	5.88								
										Speeds of Sound							
Hurly (1999)	171	210−475	0.10−1.51	0.03			0.07			Jarvis et al. (1996)	71	282−322	0.12−3.10	0.63			0.36
Hurly et al. (2003)	181	225−375	0.08−3.18	0.12			0.08										
										Enthalpies of Vaporization							
Kim (1974)	7	269−292		19.6						Pace and Aston (1948)	8	180−195		0.67			
										Enthalpy Differences							
Hejmadi et al. (1977)	33	292−293	3.00−6.43	0.11						Kim (1974)	103	285−295	2.59−3.05	2.71			0.66
										Second Virial Coefficients							
Bell et al. (1992)	3	290−310		2.26			1.93			Pace and Aston (1948)	9	180−298		5.51			20.2
Dantzler and Knobler (1969)	2	323−373					11.8										
										Ideal Gas Isobaric Heat Capacities							
Chen et al. (1975b)[c]	6	200−500		0.04			0.05			Marsh et al. (1994)[c]	118	175−5000		0.25			0.15
Hurly (1999)	14	210−475		0.38			0.07										
										1,1-Dichloro-1-fluoroethane (R-141b)							
										pρT Data							
Defibaugh and Moldover (1997)	70	279−369	0.10−6.11		0.06					Matsuo et al. (1994)	109	298−348	0.10−99.8		0.03		
Duarte-Garza et al. (1997)	73	180−400	0.12−69.5	0.12	0.09					Sousa et al. (1996)	90	260−320	0.10−23.0		0.26		
Maezawa et al. (1991b)	24	280−400	0.50−2.01		0.45					Weber (1991)	47	333−393	0.11−0.92	0.03			
Malhotra and Woolf (1994)	77	278−338	2.40−99.2		0.18												
										Vapor Pressures							
Defibaugh et al. (1993)	57	254−356	0.01−0.45	0.09						Tanaka et al. (1992)	3	298−313	0.08−0.14	4.64			
Duarte-Garza et al. (1997)	18	250−450	0−2.79	0.08						Weber (1991)	19	329−418	0.22−1.66	0.08			
Maezawa et al. (1991b)	35	200−400	0−1.18	22.2						Weber (1992)	30	271−312	0.03−0.13	0.06			
										Saturated Liquid Densities							
Defibaugh et al. (1993)	10	279−368			0.03					Malhotra and Woolf (1994)	8	278−338			0.12		
Kumagai and Takahashi (1993)	9	273−353			0.04					Matsuo et al. (1994)	11	298−348			0.00		
Maezawa et al. (1991b)	35	200−400			0.37					Sousa et al. (1994)	7	273−303			0.05		
										Speeds of Sound							
Goodwin and Moldover (1991)	42	260−315	0−0.07	0.00						Takagi and Hongo (1993)	180	283−373	0.05−52.0		0.21		
										Second Virial Coefficients							
Duarte-Garza et al. (1977)	1	400		0.38						Goodwin and Moldover (1991)	18	260−393		2.03			
										Ideal Gas Isobaric Heat Capacities							
Goodwin and Moldover (1991)	5	260−315		0.03						Marsh et al. (1994)[c]	119	170−5000		0.15			0.47
Smith et al. (1952)[c]	3	305−600		0.31			0.81										

Table 9 (Continued)

		temp and pressure ranges		average absolute deviations (AAD/%)^b								temp and pressure ranges		average absolute deviations (AAD/%)^b					
							supercritical fluid										supercritical fluid		
reference	no.	T/K	p/MPa	gas	liq	crit reg	LD	MD	HD	reference	no.	T/K	p/MPa	gas	liq	crit reg	LD	MD	HD
1-Chloro-1,1-difluoroethane (R-142b)																			
pρT Data																			
Cherneeva (1958)	42	275−369	0.14−1.40	3.01						Riedel (1941)	18	258−313	0.06−0.28	0.10					
Dressner and Bier (1993)	114	373−423	0.21−57.6	0.10		1.02	0.30	1.23	0.64	Sousa et al. (1992a)	47	293−403	0.38−17.5	12.8	0.09				
Fukushima and Watanabe (1992)	63	354−464	1.24−5.73	0.80	0.41	3.68	0.58	1.55	0.34	Strom and Gren (1993)	19	264−323	0.50−1.51		0.27				
Maezawa et al. (1991a)	6	320−360	1.00−2.00		0.22					Takahashi et al. (1987)	96	298−423	0.10−5.09	1.51		3.56	1.85	2.12	
Mears et al. (1955)	17	352−427	1.25−4.16	3.39			4.13			Yada et al. (1991)	70	347−443	1.21−9.37	0.76	0.23	4.88	0.89	0.14	0.33
Vapor Pressures																			
Cherneeva (1958)	21	213−410	0−4.19	1.09						Maezawa et al. (1991a)	12	320−400	0.63−3.39	0.46					
Fukushima and Watanabe (1992)	35	273−410	0.15−4.04	0.25						Mears et al. (1955)	19	248−390	0.05−2.99	1.54					
Kleiber (1994)	6	268−298	0.12−0.34	0.09						Riedel (1941)	12	213−307	0−0.44	0.52					
Kubota et al. (1990)	6	263−338	0.10−1.00	0.92						Silva and Weber (1993)	36	225−285	0.01−0.22	0.06					
Lee et al. (1998)	3	295−315	0.31−0.55	0.11						Yada et al. (1991)	69	297−410	0.32−4.04	1.54					
Saturated Liquid Densities																			
Cherneeva (1958)	15	213−366			1.43					Riedel (1941)	7	194−303			0.12				
Fukushima and Watanabe (1992)	11	392−410			0.87	1.89				Tanikawa et al. (1992)	18	354−410			0.61	1.78			
Kumagai and Takahashi (1990)	9	273−353			11.3					Valtz et al. (1986)	4	298−373			0.43				
Kumagai and Takahashi (1993)	9	273−353			0.39					Yada et al. (1991)	4	347−399			0.24				
Maezawa et al. (1991a)	36	210−400			0.32														
Saturated Vapor Densities																			
Cherneeva (1958)	18	217−369		1.14						Tanikawa et al. (1992)	12	396−410		0.50		1.64			
Fukushima and Watanabe (1992)	3	407−409		0.10		2.21				Yada et al. (1991)	3	358−396		1.27					
Mears et al. (1955)	8	303−389		3.27															
Isobaric Heat Capacities																			
Mears et al. (1955)	6	243−343	0.04−1.11		2.63					Riedel (1941)	10	212−295	0−0.30		0.64				
Nakagawa et al. (1993)	125	273−350	0.14−3.00		0.66					Sato and Watanabe (1994)	31	276−350	1.00−3.00		0.66				
Perlick (1937b)	28	146−292	0−0.27		2.03														
Speeds of Sound																			
Beckermann and Kohler (1993)	210	270−410	0.02−0.40	0.03						Komarov et al. (1967)	32	263−408	0.10−3.90	1.74	3.12				
Second Virial Coefficients																			
Kohler and Van Nhu (1993)	12	248−473		3.44			6.29			Schramm and Weber (1991)	4	248−296		4.68					
Beckermann and Kohler (1995)	8	270−410		0.96						Schramm et al. (1992)	4	296−473		3.56			6.30		
Ideal Gas Isobaric Heat Capacities																			
Beckermann and Kohler (1995)	16	270−410		0.34						Mears et al. (1955)^c	9	250−1000		0.60			0.29		
Marsh et al. (1994)^c	124	145−5000		0.04			0.13			Smith et al. (1952)^c	4	264−600		0.57			0.34		
Octafluoropropane (R-218)																			
pρT Data																			
Bouchot and Richon (1997)	908	253−333	0.10−14.2	0.81	0.16					Defibaugh and Moldover (1997)	987	247−371	1.00−6.50		0.02	3.28	0.78	0.35	0.05
Brown (1963)	28	333−439	1.80−5.87	3.17		8.68	1.72	1.31											
Vapor Pressures																			
Bouchot and Richon (1997)	10	253−333	0.20−2.04	0.31						Mousa (1978)	13	330−345	1.91−2.66	0.75					
Brown (1963)	12	213−341	0.03−2.44	0.92						Pace and Plaush (1967)	10	194−237	0−0.10	0.67					
Crowder et al. (1967)	8	182−237	0−0.11	2.05						Vladimirov and Shvets (1989)	10	263−343	0.29−2.53	0.13					
Leu and Robinson (1992)	3	323−343	1.65−2.55	1.50															
Saturated Liquid Densities																			
Bouchot and Richon (1997)	5	253−333			0.16					Brown (1963)	9	223−323			0.32				

									Saturated Vapor Densities										
Bouchot and Richon (1997)	5	253−333		1.24						Brown (1963)	9	223−323		0.56					
									Saturation Liquid Heat Capacities										
Pace and Plaush (1967)	36	126−233		0.56															
									Isobaric Heat Capacities										
Masi et al. (1954)	12	243−363	0.03−0.15	0.70			0.17			Ponomareva and Romanov (1989)	32	217−329	1.00−10.0		25.6				
									Speeds of Sound										
Beljeva et al. (1997)	100	242−341	0.77−16.2		0.35					Vacek et al. (2001)	64	254−303	0.01−0.40	0.48					
									Second Virial Coefficients										
Dantzler and Knobler (1969)	2	323−373		4.19			0.02												
									Ideal Gas Isobaric Heat Capacities										
Marsh et al. (1994)[c]	127	130−5000		0.16			0.11			Masi et al. (1954)	4	243−363		0.24			0.31		
									1,1,1,3,3-Pentafluoropropane (R-245fa)										
									pρT Data										
Bobbo et al. (2003)	200	283−343	0.20−25.2		0.06					Grebenkov et al. (2004)	355	257−437	0.03−9.23	1.18	0.10	3.58	1.32	0.93	
Defibaugh and Moldover (1997)	1041	252−372	0.49−6.49		0.02					Sotani and Kubota (1999)	109	298−343	0.15−91.1	0.64	0.07				
Di Nicola (2001)	32	313−367	0.22−0.61	0.59															
									Vapor Pressures										
Bobbo et al. (2001)	6	293−313	0.12−0.25	0.19						Pan et al. (2006)	40	253−403	0.02−2.35	0.14					
Defibaugh and Moldover (1997)	28	252−372	0.02−1.22	0.57						Sotani and Kubota (1999)	32	293−426	0.13−3.60	0.98					
Di Nicola (2001)	51	265−352	0.04−0.76	0.16						Wang and Duan (2004)	79	255−394	0.02−1.95	0.23					
Grebenkov et al. (2004)	108	242−427	0−3.64	0.36															
									Saturated Liquid Densities										
Beyerlein et al. (1993)	6	284−358			0.66					Defibaugh and Moldover (1997)	28	252−372			0.03				
Bobbo et al. (2003)	8	283−343			0.08					Grebenkov et al. (2004)	33	256−427			0.20	0.85			
									Saturated Vapor Densities										
Grebenkov et al. (2004)	28	267−427		1.65		0.92													
									Isobaric Heat Capacities										
Hwang et al. (1992)	3	308−323	0.21−0.34		4.61														
									Speeds of Sound										
Grebenkov et al. (2004)	121	293−353	0.18−7.12		0.11														
									Ideal Gas Isobaric Heat Capacities										
Scott (2004)	4	290−350		0.17															
									Fluoromethane (R-41)										
									pρT Data										
Bominaar et al. (1987)	256	294−343	0.14−29.3	0.65	0.13	3.05	0.09	0.23	0.10	Holcomb et al. (1998)	24	274−296	2.20−3.73	3.60	0.30				
Cawood and Patterson (1932)	15	273−318	0.13−0.41	4.57			15.0			Magee et al. (1998)	445	132−400	2.90−35.4		0.03	0.58	0.09	0.08	0.02
David et al. (1952)	50	323−348	2.20−16.3			1.17	0.58	0.32	0.84	Michels et al. (1952b)	103	273−423	0.82−16.7	0.09		0.35	0.17	0.28	
Demiriz et al. (1993)	67	257−338	0.19−62.4		0.59	3.97	0.27		0.52										
									Vapor Pressures										
Biswas et al. (1989)	34	283−317	2.66−5.85	0.44						Grosse et al. (1940)	6	140−195	0−0.10	2.47					
Bominaar et al. (1987)	22	298−316	3.84−5.76	0.35						Holcomb et al. (1998)	20	252−312	1.10−5.24	0.24					
Demiriz et al. (1993)	28	253−314	1.14−5.47	0.33						Magee et al. (1998)	31	170−317	0.02−5.86	0.09					
Duarte-Garza and Magee (1999)	25	130−250	0−1.03	0.85						Michels and Wassenaar (1948)	34	164−288	0.01−3.05	0.25					
Fonseca and Lobo (1989)	3	161−195	0.01−0.11	0.50						Oi et al. (1983)	130	132−213	0−0.25	0.20					
									Saturated Liquid Densities										
Biswas et al. (1989)	6	286−313			0.06					Magee et al. (1998)	13	131−309			0.10				
Cawood and Patterson (1932)	13	293−317			2.50	3.15				Shinsaka et al. (1985)	25	140−218			0.46				
Grosse et al. (1940)	5	143−213			0.13														

Table 9 (Continued)

reference	no.	temp and pressure ranges		average absolute deviations (AAD/%)^b						reference	no.	temp and pressure ranges		average absolute deviations (AAD/%)^b				
							supercritical fluid										supercritical fluid	
		T/K	p/MPa	gas	liq	crit reg	LD	MD	HD			T/K	p/MPa	gas	liq	crit reg	LD	MD
Fluoromethane (R-41) (continued)																		
Saturated Vapor Densities																		
Biswas et al. (1989)	5	269−314		3.21						Cawood and Patterson (1932)	13	293−317		12.7				
Saturation Liquid Heat Capacities																		
Magee et al. (1998)	113	134−314		0.72														
Isochoric Heat Capacities																		
Magee et al. (1998)	122	148−343	3.28−32.8	8.40	0.43	1.66	7.54	1.65	0.33									
Speeds of Sound																		
Scott et al. (1998)	37	250−350	0.10−3.44	0.09			0.09											
Second Virial Coefficients																		
Bignell and Dunlop (1993)	3	290−310		1.54						Hamann and Pearse (1951)	7	293−353		2.16			0.89	
D'Amore et al. (2003)	9	303−343		0.69			1.05			Lamp et al. (2002)	3	296−463		1.25			1.10	
Demiriz et al. (1993)	9	298−339		0.36			1.85			Michels et al. (1952b)	7	273−423		6.16			24.2	
Ideal Gas Isobaric Heat Capacities																		
Barho (1965)^c	17	200−1000		0.19			0.41			Marsh et al. (1994)^c	127	130−5000		0.26			0.21	

^{a} Key: no., number of points; crit reg, 0.98 < T/T_c < 1.1 and 0.7 < ρ/ρ_c < 1.4; LD, ρ/ρ_c < 0.6; MD, 0.6 < ρ/ρ_c < 1.5; HD, ρ/ρ_c > 1.5. ^{b} Enthalpy differences are given in kJ·mol^{-1}. ^{c} Ideal gas isobaric heat capacities calculated from statistical thermodynamics.

several data sets show consistent results to within 50 K of the critical temperature, and deviations from the equation of state are 0.75 % (with agreement at 0.5 % near the critical point).

The equation agrees with reliable data for the liquid-phase isobaric heat capacity to within 1 %. These data range from the triple point up to 310 K and are all located on the saturation boundary. There are no caloric data available at high pressures. Above 280 K, the scatter in the data increases dramatically, but the data of Low and Moelwyn-Hughes (1962) show that the inconsistency is likely not a problem with the equation of state. Isobaric heat capacities in the vapor phase are available above 330 K, and most are represented within 2 %, with deviations of 0.2 % from the data of Pennington and Kobe (1957). These data agree well with the ideal gas isobaric heat capacities of Ding et al. (1997). Deviations from the liquid-phase speed of sound data show that there is a slight systematic offset in the equation, although the deviations of most of the data points are less than 1 %. The data cover a limited range from (250 to 325) K. Laesecke (2006) measured speeds of sound and densities in the liquid phase from (278 to 313) K after this work was completed as a check on the reliability of the equation. Comparisons showed that the average absolute deviations of the equation from the new measurements were 0.13 % in speed of sound and 0.11 % in density. The scatter in the second virial coefficients is quite large (about 20 %). The equation was fitted to the more consistent data, with most of these data points represented to within 5 %. Comparisons with the enthalpy data of Yerlett and Wormald (1986) show differences typically within 1 kJ·mol^{-1}.

The estimated uncertainties in the equation of state are 0.1 % in the saturated liquid density between (280 and 310) K, 0.5 % in density in the liquid phase below 380 K and 1 % in density elsewhere, including all states at pressures above 100 MPa. The uncertainties in vapor pressure are 0.5 % above 270 K (0.25 % between 290 K and 390 K), and the uncertainties in heat capacities and speeds of sound are 1 %. The uncertainties in caloric properties and sound speeds may be higher at pressures above the saturation pressure and at temperatures above 320 K in the liquid phase and at supercritical conditions.

Carbon Monoxide. Experimental measurements for carbon monoxide and their deviations from the equation of state are summarized in Table 9 and shown in Figures 3 and 4. The coefficients of the equation relied heavily on the data of Barreiros et al. (1982b) in the liquid phase at low temperatures and the data of Michels et al. (1952a) at supercritical states. Deviations from the data of Barreiros et al. are 0.13 % in density between (82 and 125) K and at pressures to 140 MPa (the full limits of the experimental data). Deviations for the data of Michels et al. are 0.12 % for pressures less than 100 MPa and rise to 1 % at 200 MPa. The maximum deviation at pressures less than 100 MPa is 0.4 %. It was not possible to completely remove the curvature in the equation at temperatures such as 340 K as shown by comparisons with the data of Michels et al. Both the polar and the nonpolar functional forms were tried, with the nonpolar form resulting in a better fit, although not optimal as could be achieved with a modified functional form (by changing the temperature exponents in the terms as was done with R-41 in this work). There are only a few measurements of carbon monoxide in the critical region (Goodwin, 1983), and the uncertainties of these data are not small enough to accurately represent this region.

The equation of state represents most of the vapor pressure measurements to within 0.2 %, with several outlying sets represented within 0.6 %. At temperatures above 90 K, the data

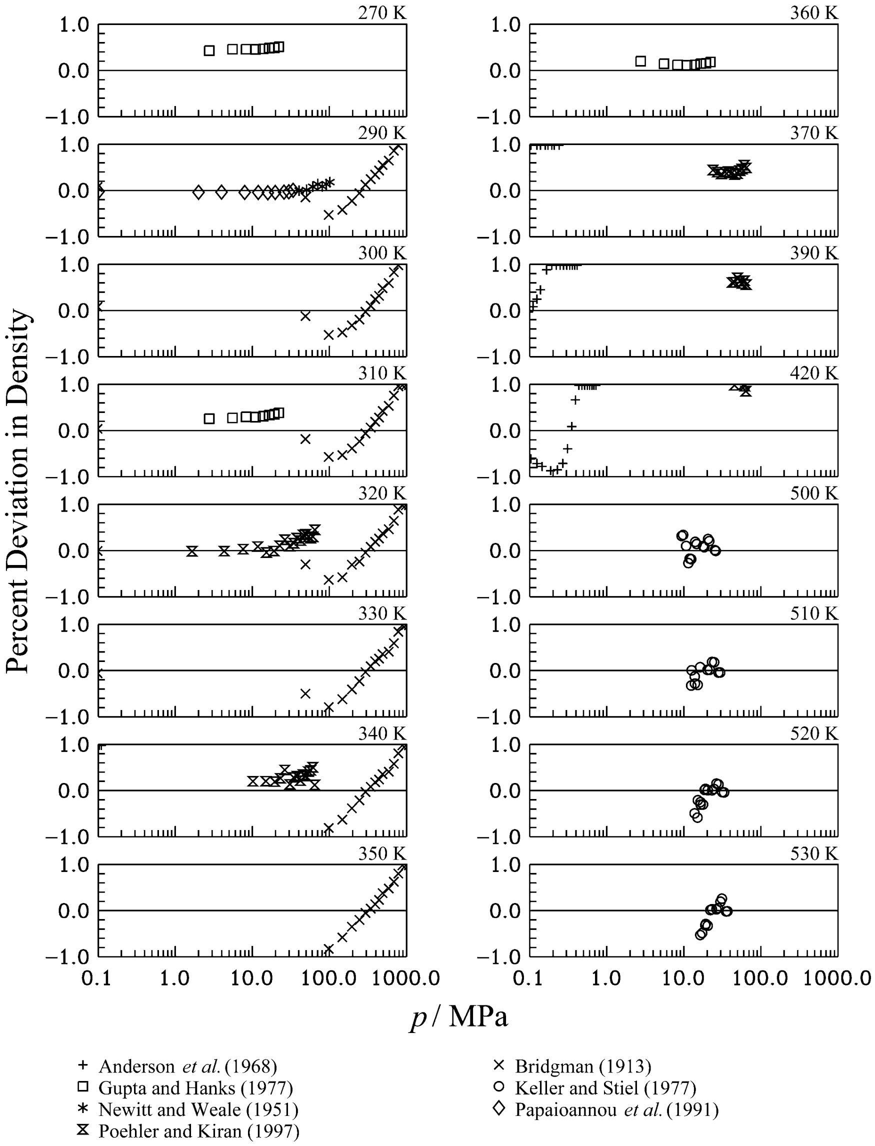

Figure 1. Acetone: comparisons of densities calculated with the equation of state to experimental data.

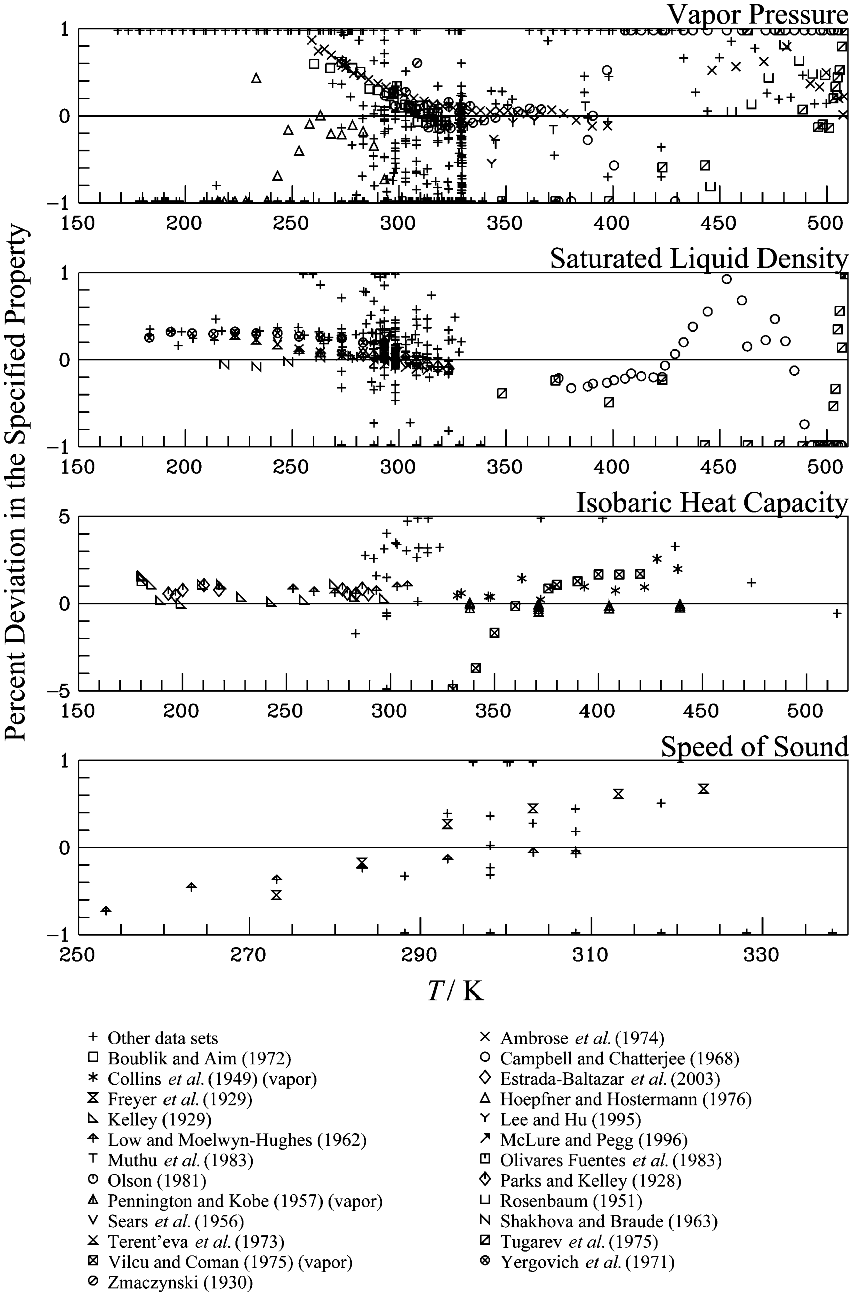

Figure 2. Acetone: comparisons of vapor pressures, saturated liquid densities, isobaric heat capacities, and speeds of sound calculated with the equation of state to experimental data.

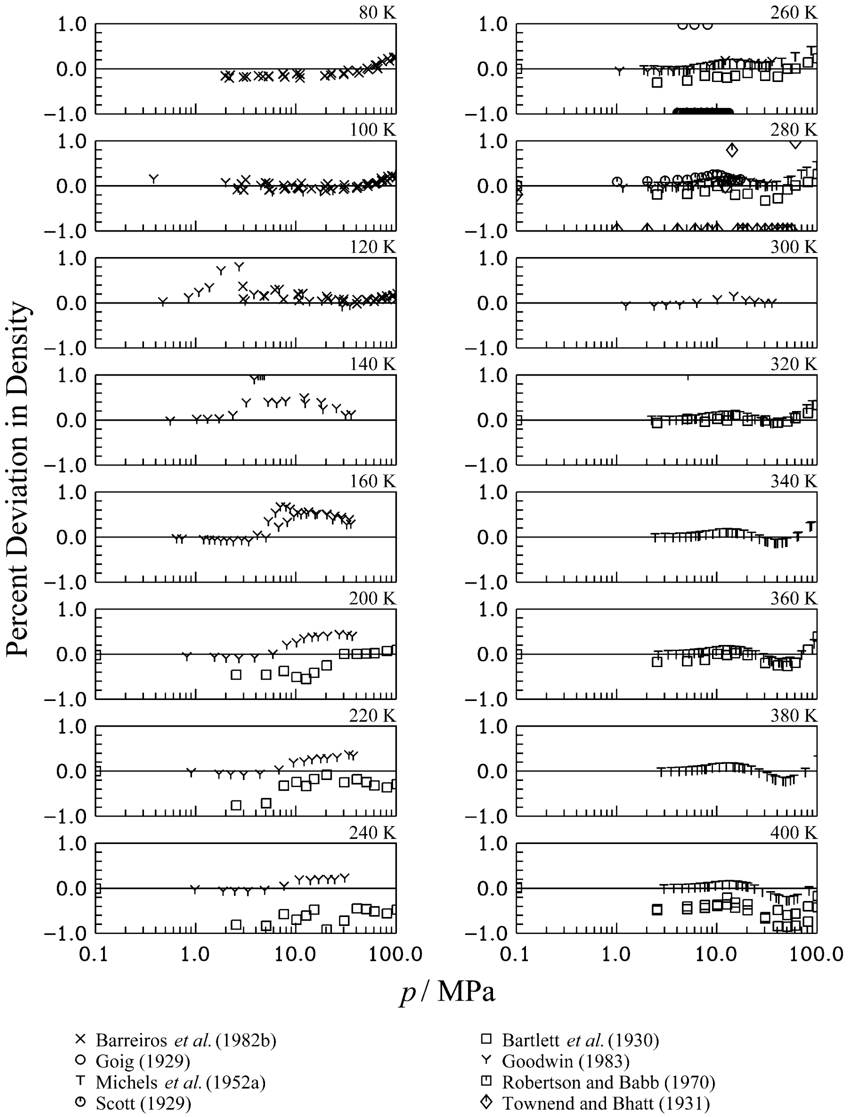

Figure 3. Carbon monoxide: comparisons of densities calculated with the equation of state to experimental data.

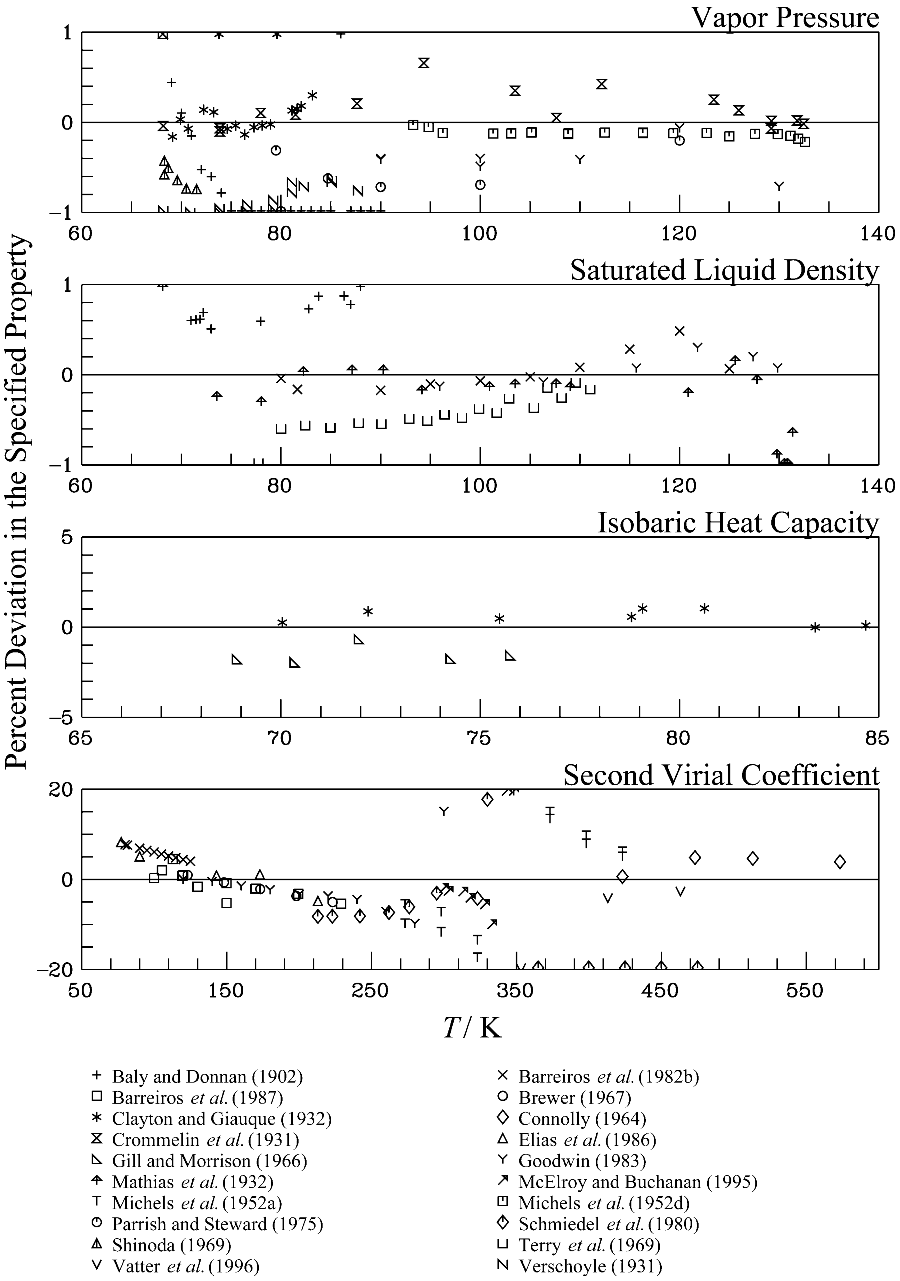

Figure 4. Carbon monoxide: comparisons of vapor pressures, saturated liquid densities, isobaric heat capacities, and second virial coefficients calculated with the equation of state to experimental data.

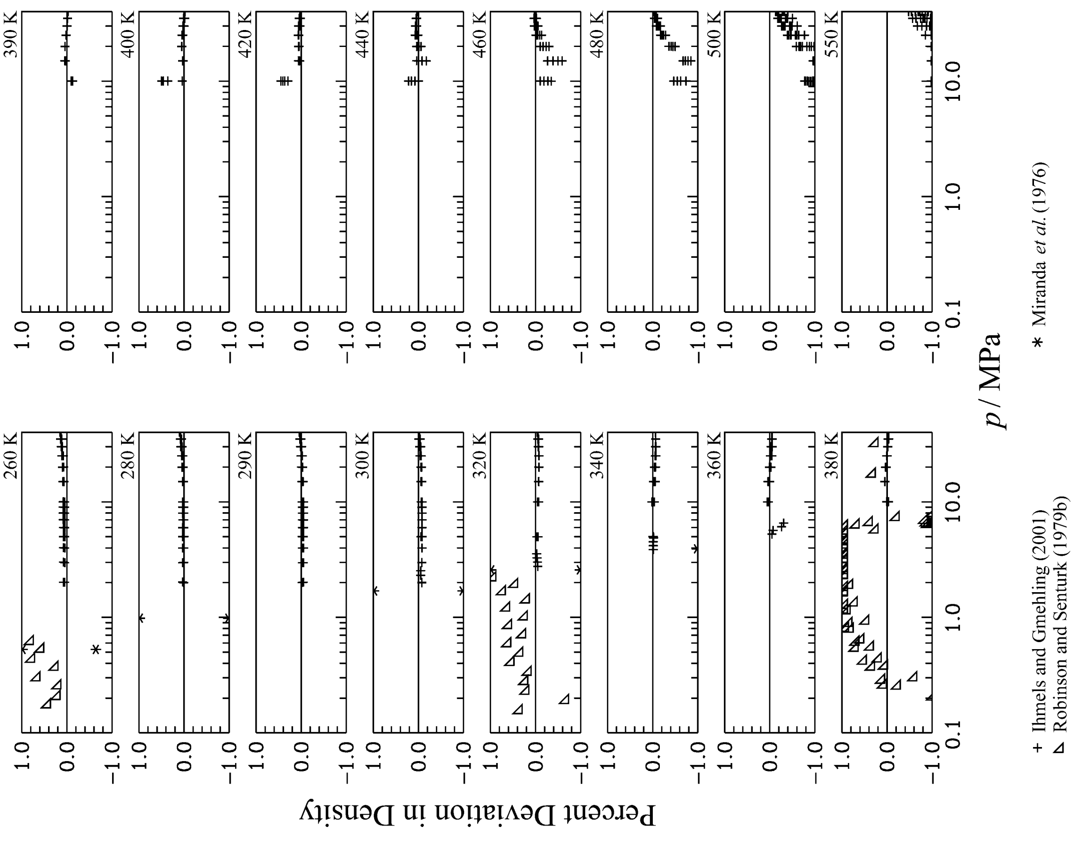

Figure 5. Carbonyl sulfide: comparisons of densities calculated with the equation of state to experimental data.

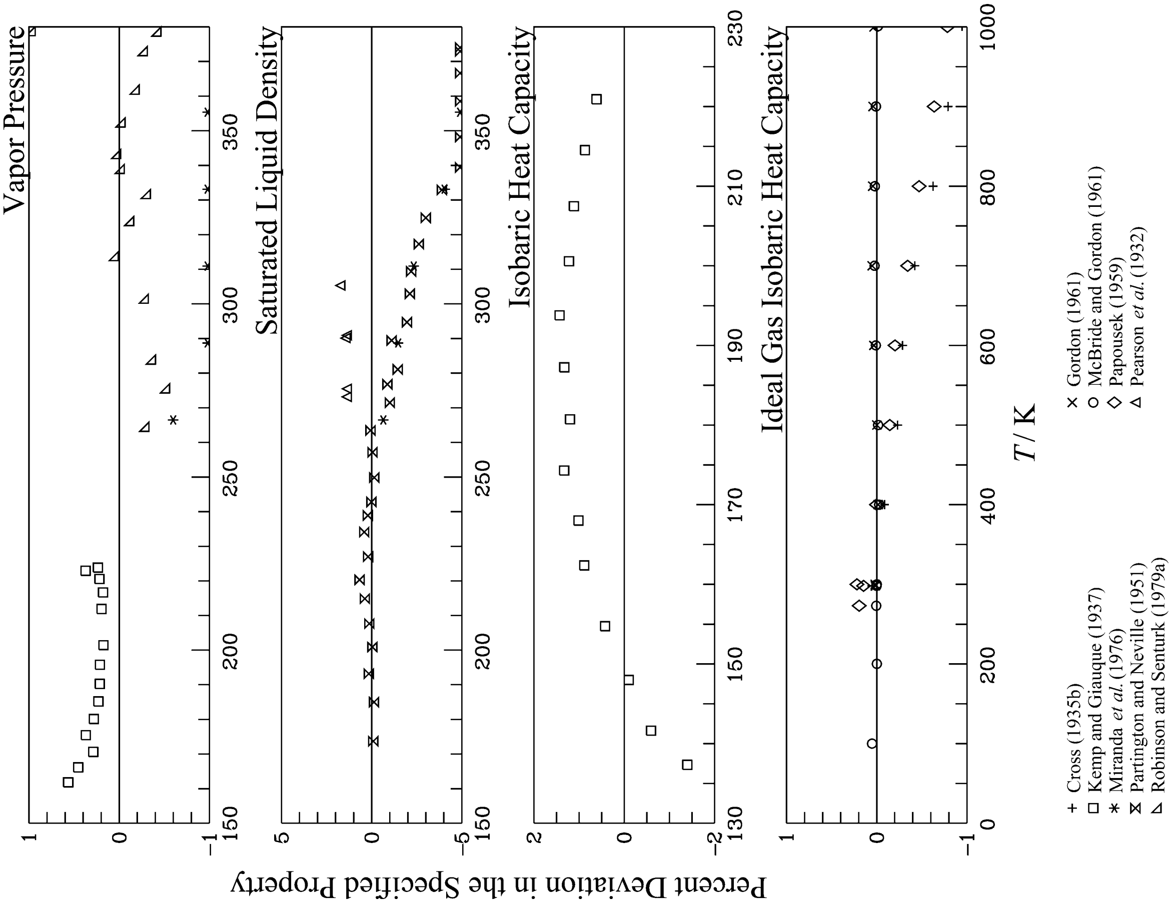

Figure 6. Carbonyl sulfide: comparisons of vapor pressures, saturated liquid densities, and isobaric heat capacities calculated with the equation of state to experimental data.

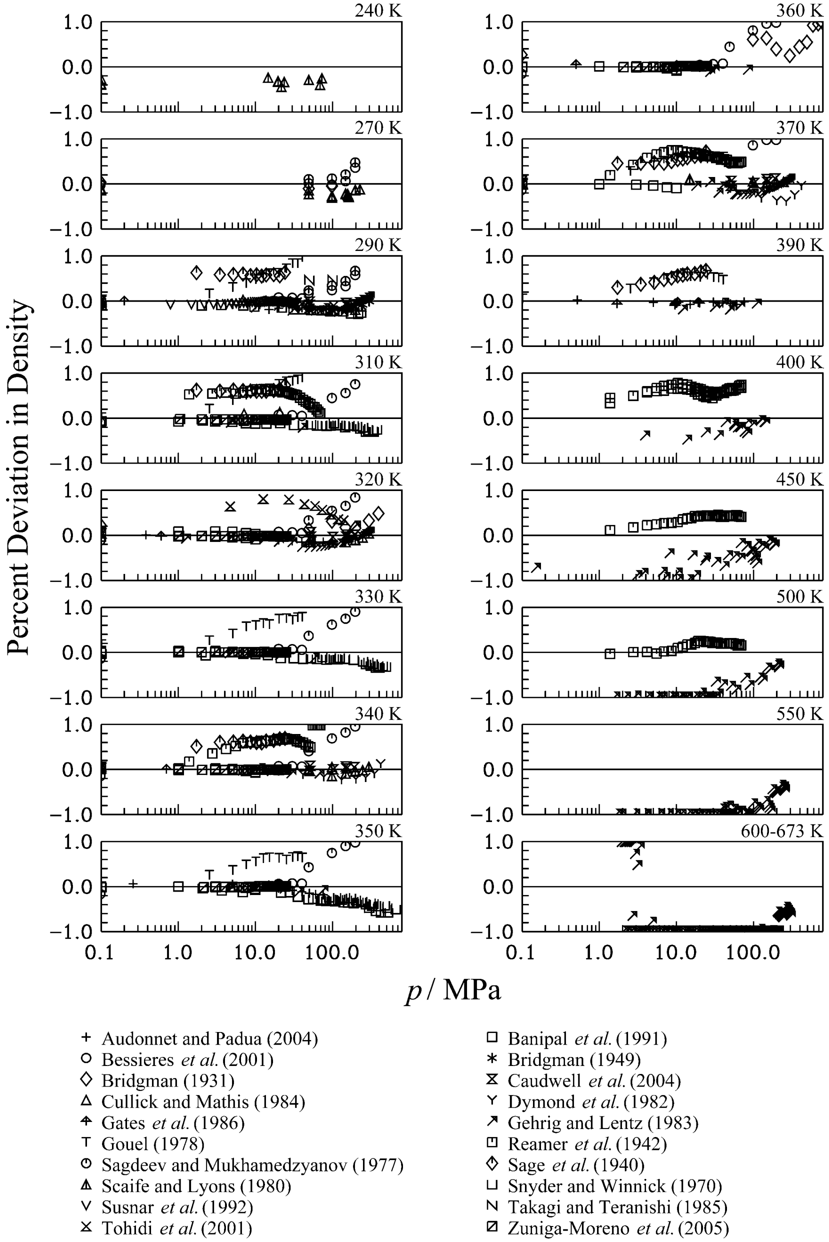

Figure 7. Decane: comparisons of densities calculated with the equation of state to experimental data.

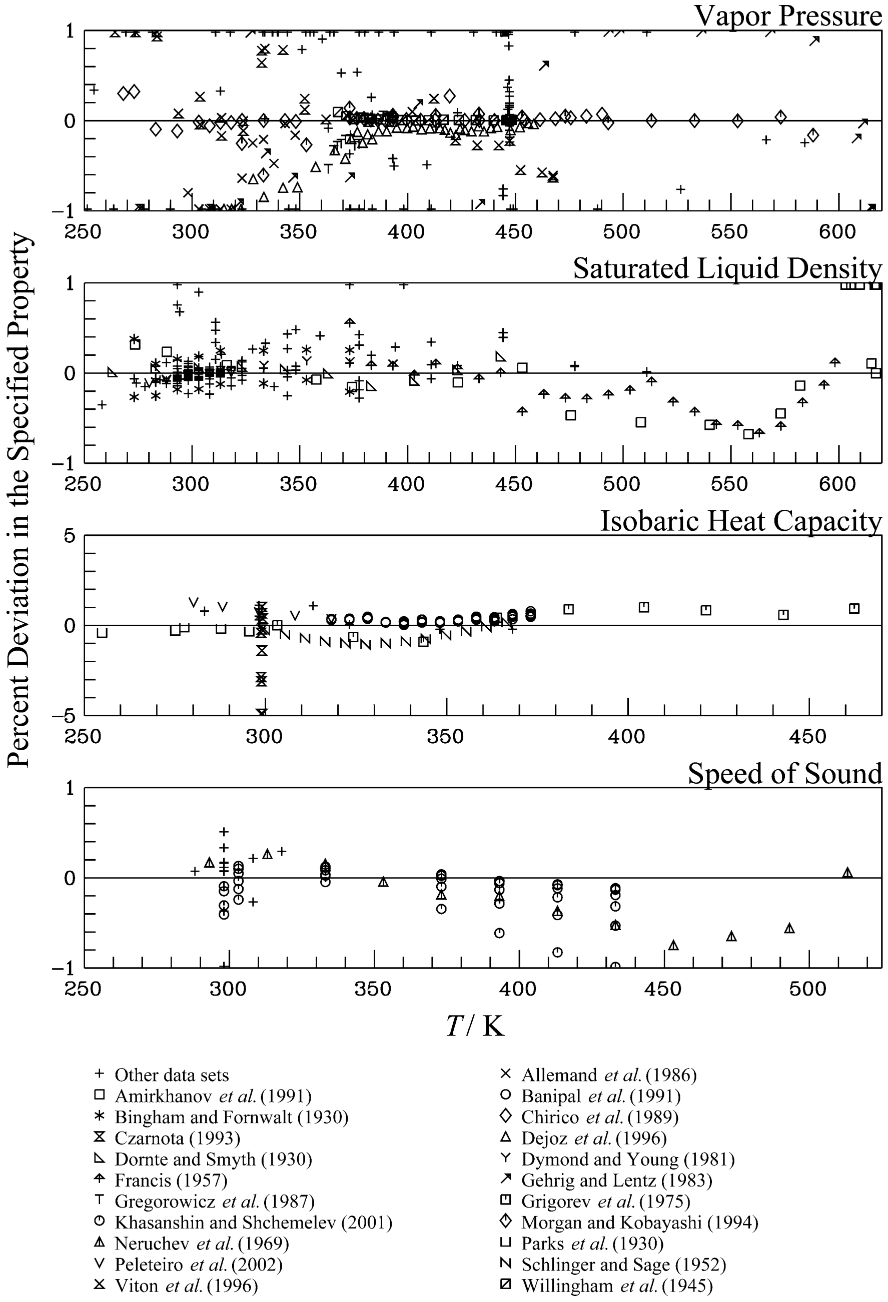

Figure 8. Decane: comparisons of vapor pressures, saturated liquid densities, isobaric heat capacities, and speeds of sound calculated with the equation of state to experimental data.

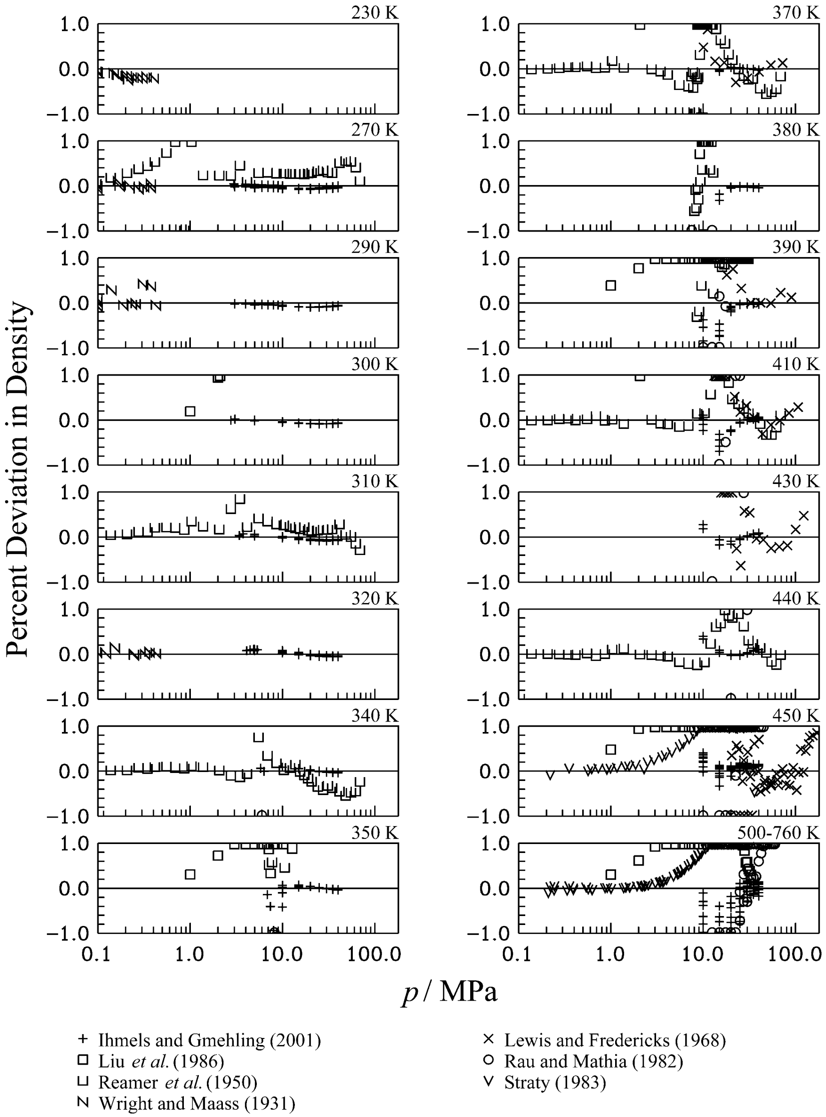

Figure 9. Hydrogen sulfide: comparisons of densities calculated with the equation of state to experimental data.

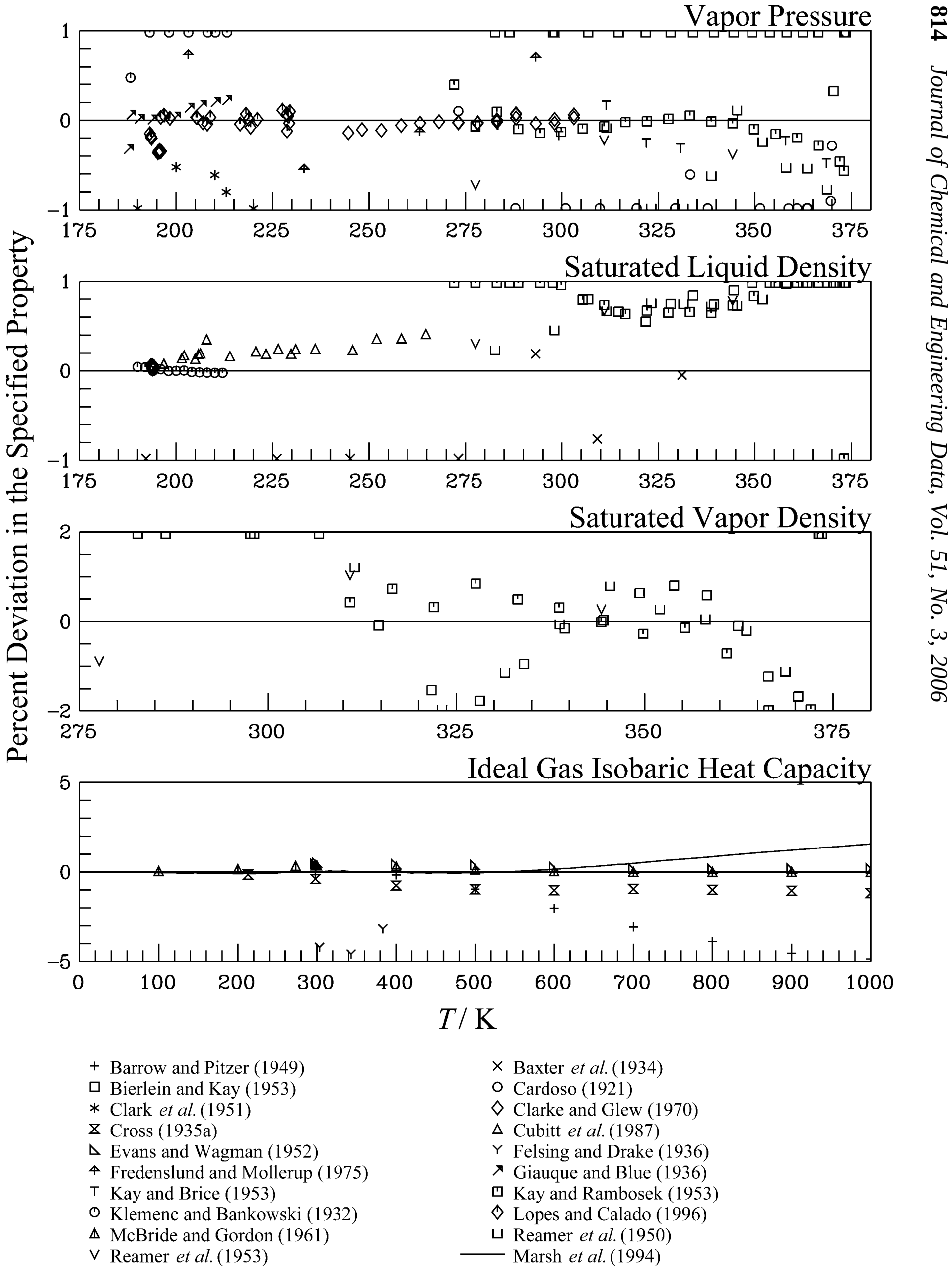

Figure 10. Hydrogen sulfide: comparisons of vapor pressures, saturated liquid and vapor densities, and isobaric heat capacities calculated with the equation of state to experimental data.

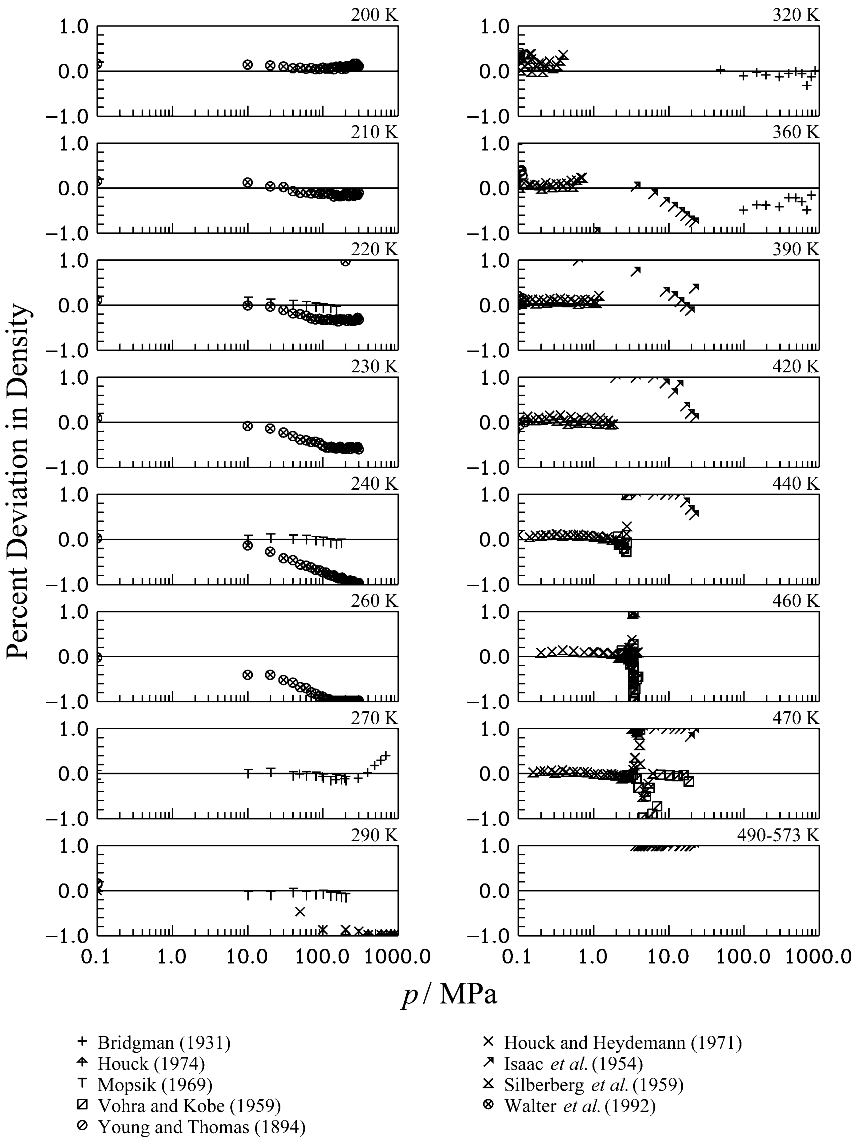

Figure 11. 2-Methylbutane (isopentane): comparisons of densities calculated with the equation of state to experimental data.

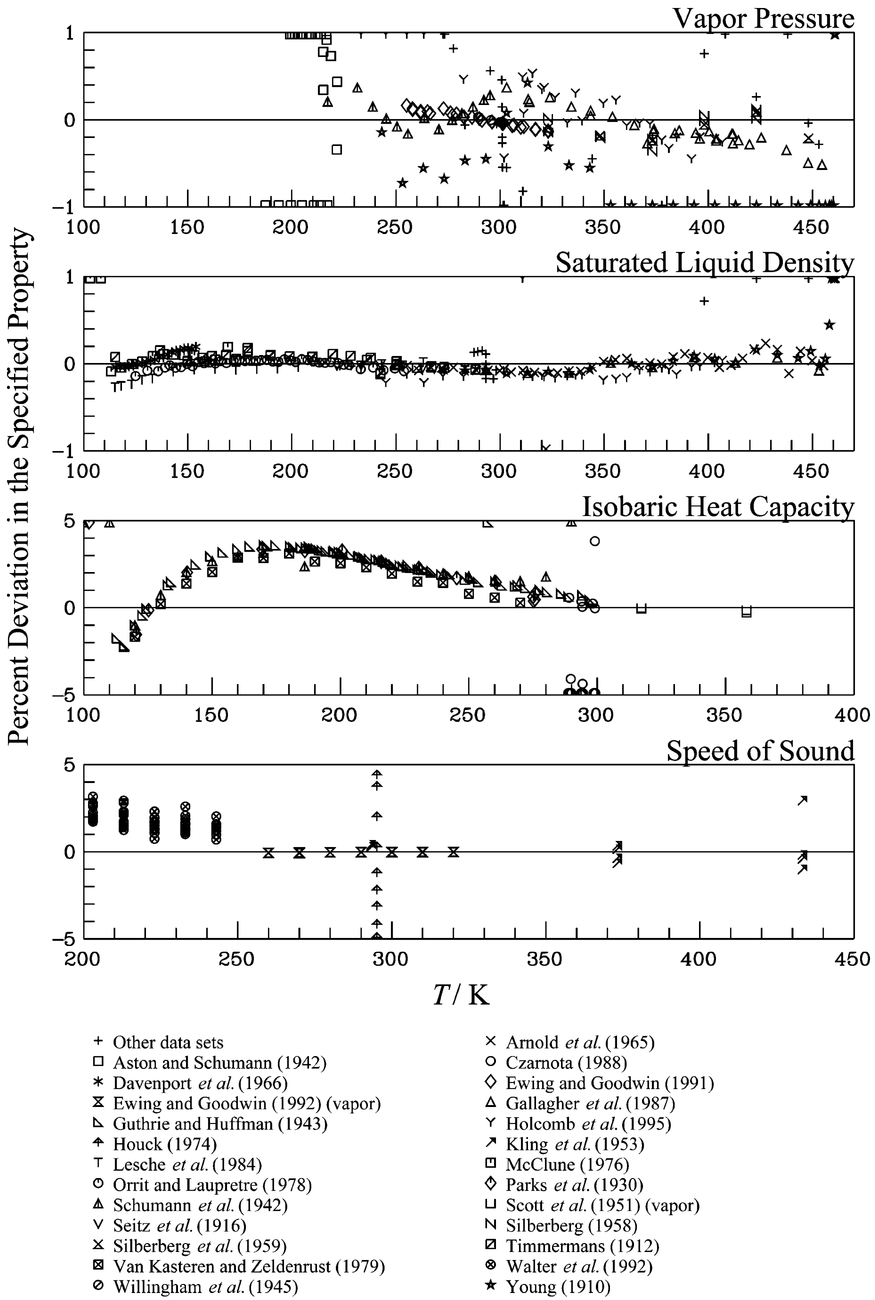

Figure 12. 2-Methylbutane (isopentane): comparisons of vapor pressures, saturated liquid densities, isobaric heat capacities, and speeds of sound calculated with the equation of state to experimental data.

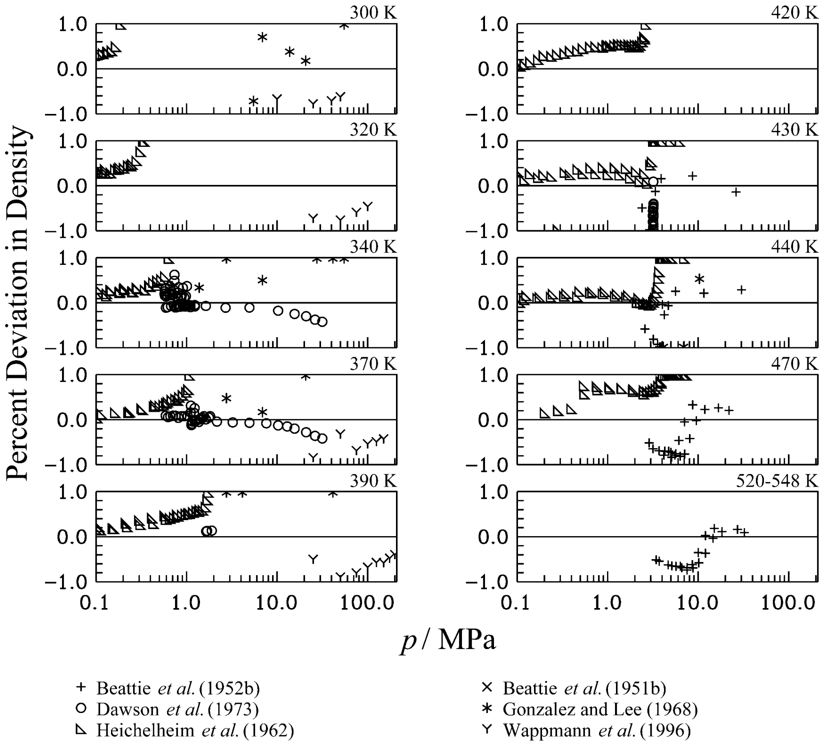

Figure 13. 2,2-Dimethylpropane (neopentane): comparisons of densities calculated with the equation of state to experimental data.

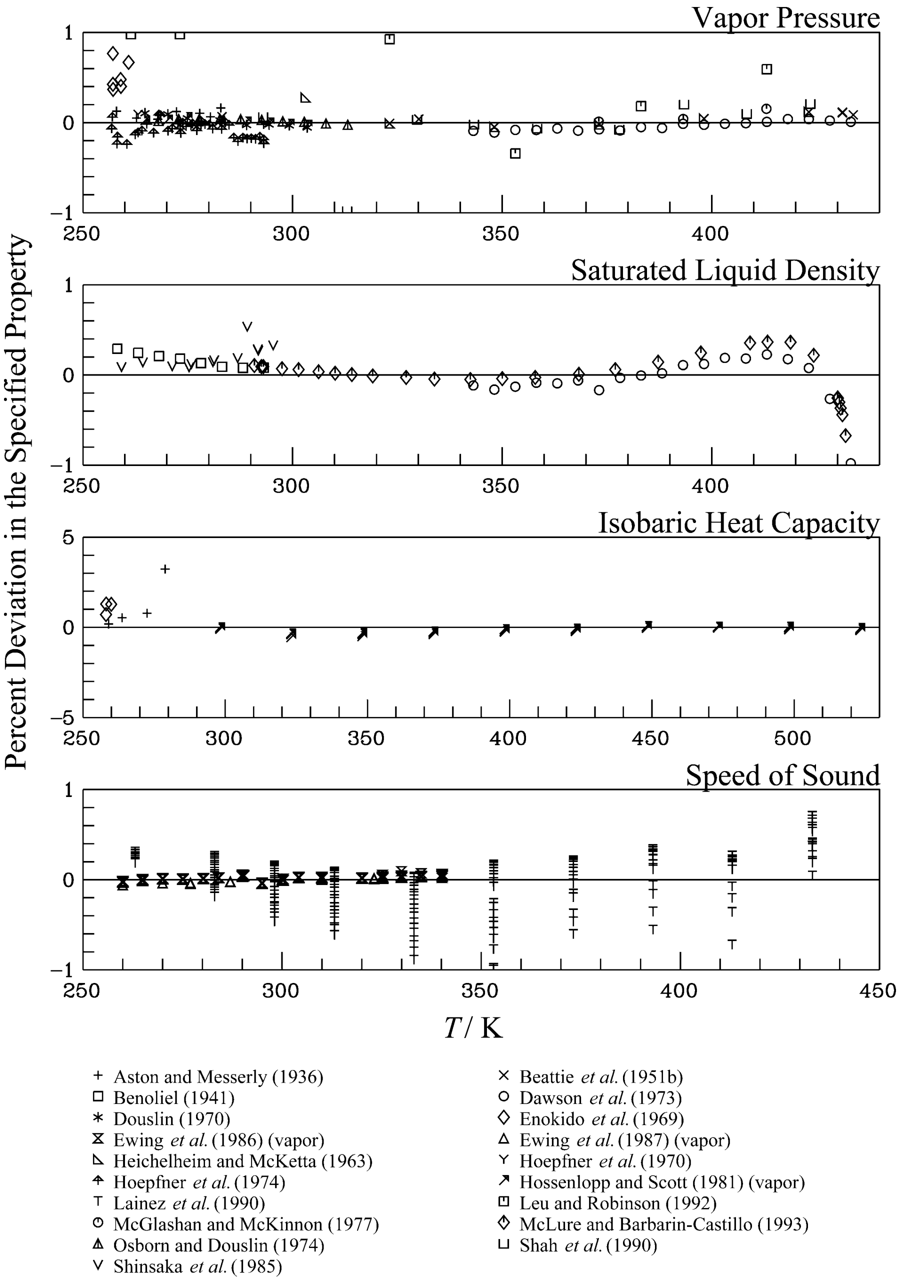

Figure 14. 2,2-Dimethylpropane (neopentane): comparisons of vapor pressures, saturated liquid densities, isobaric heat capacities, and speeds of sound calculated with the equation of state to experimental data.

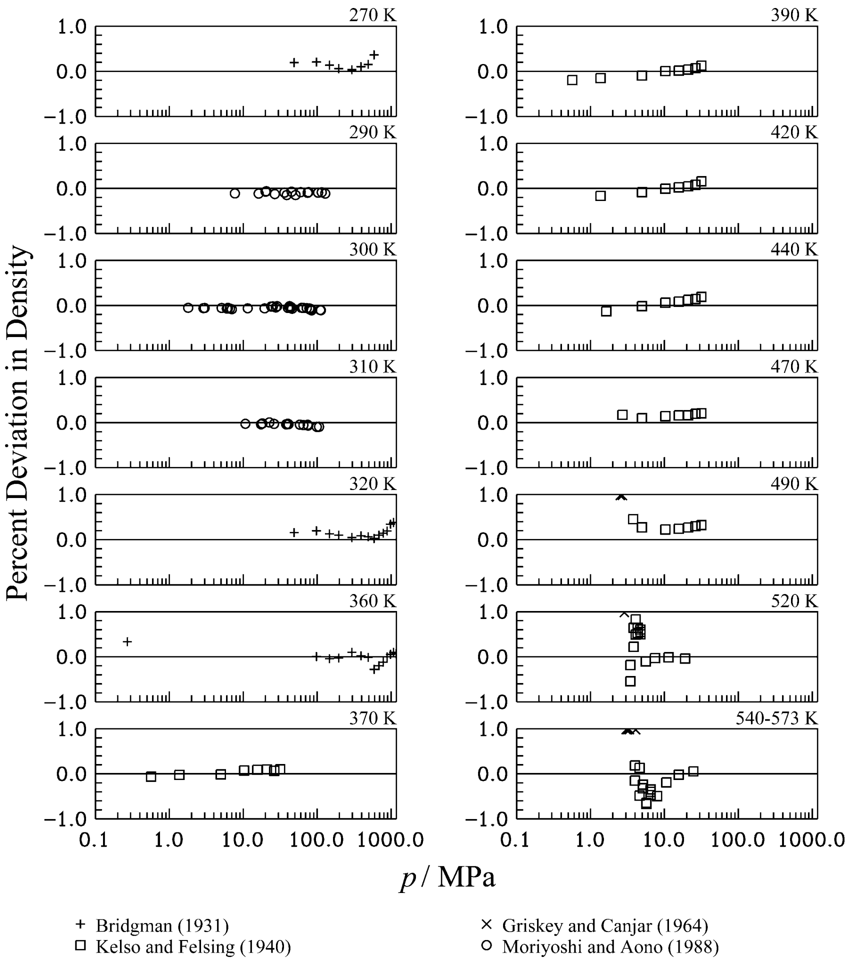

Figure 15. 2-Methylpentane (isohexane): comparisons of densities calculated with the equation of state to experimental data.

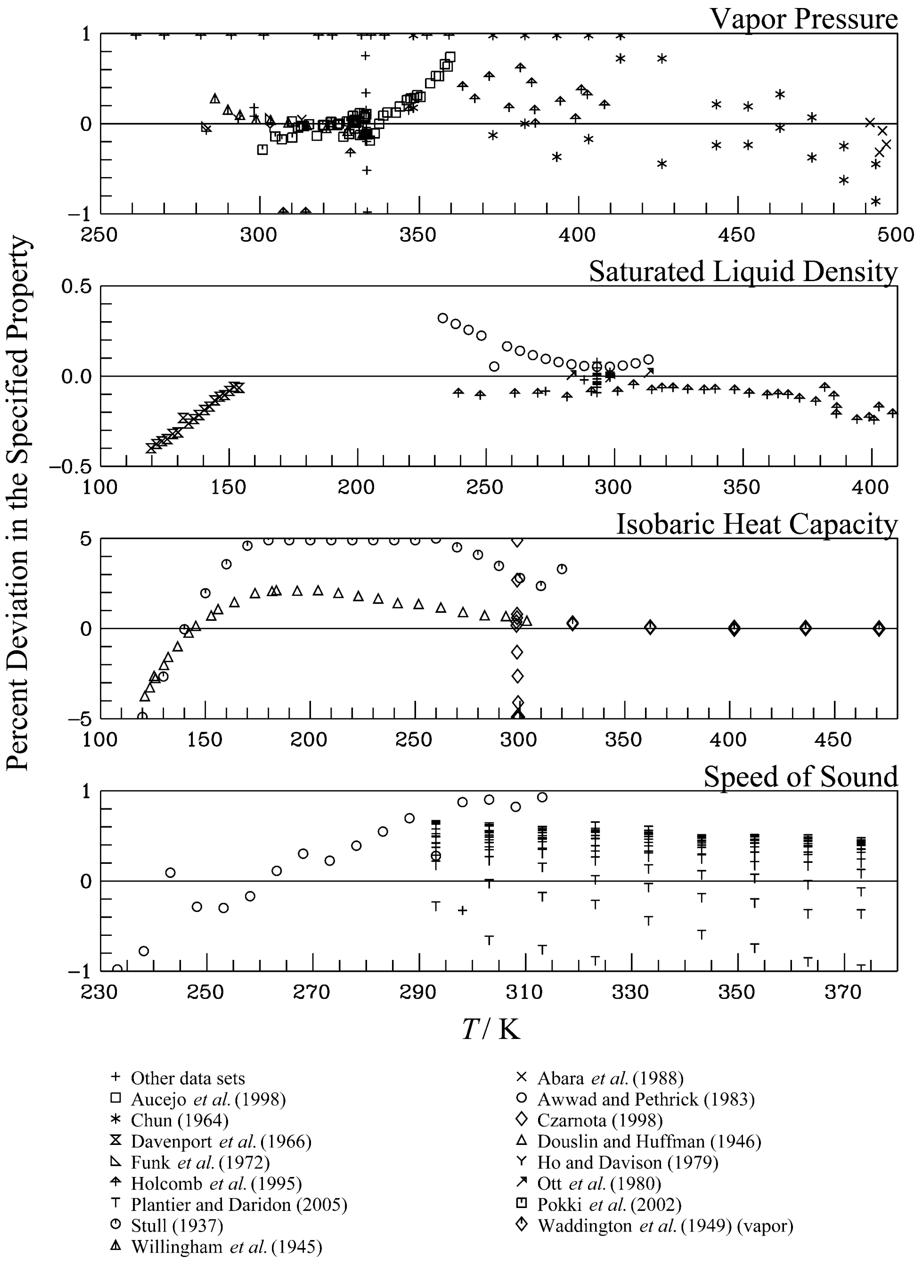

Figure 16. 2-Methylpentane (isohexane): comparisons of vapor pressures, saturated liquid densities, isobaric heat capacities, and speeds of sound calculated with the equation of state to experimental data.

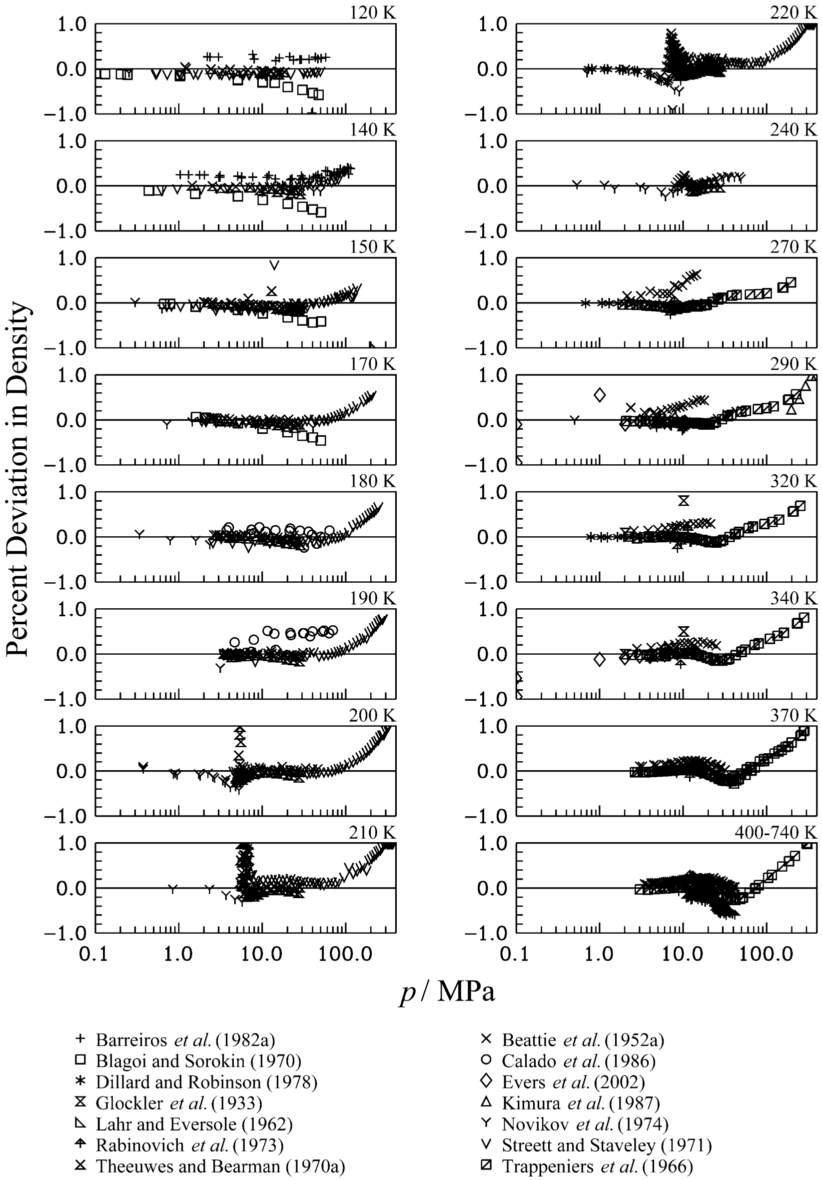

Figure 17. Krypton: comparisons of densities calculated with the equation of state to experimental data.

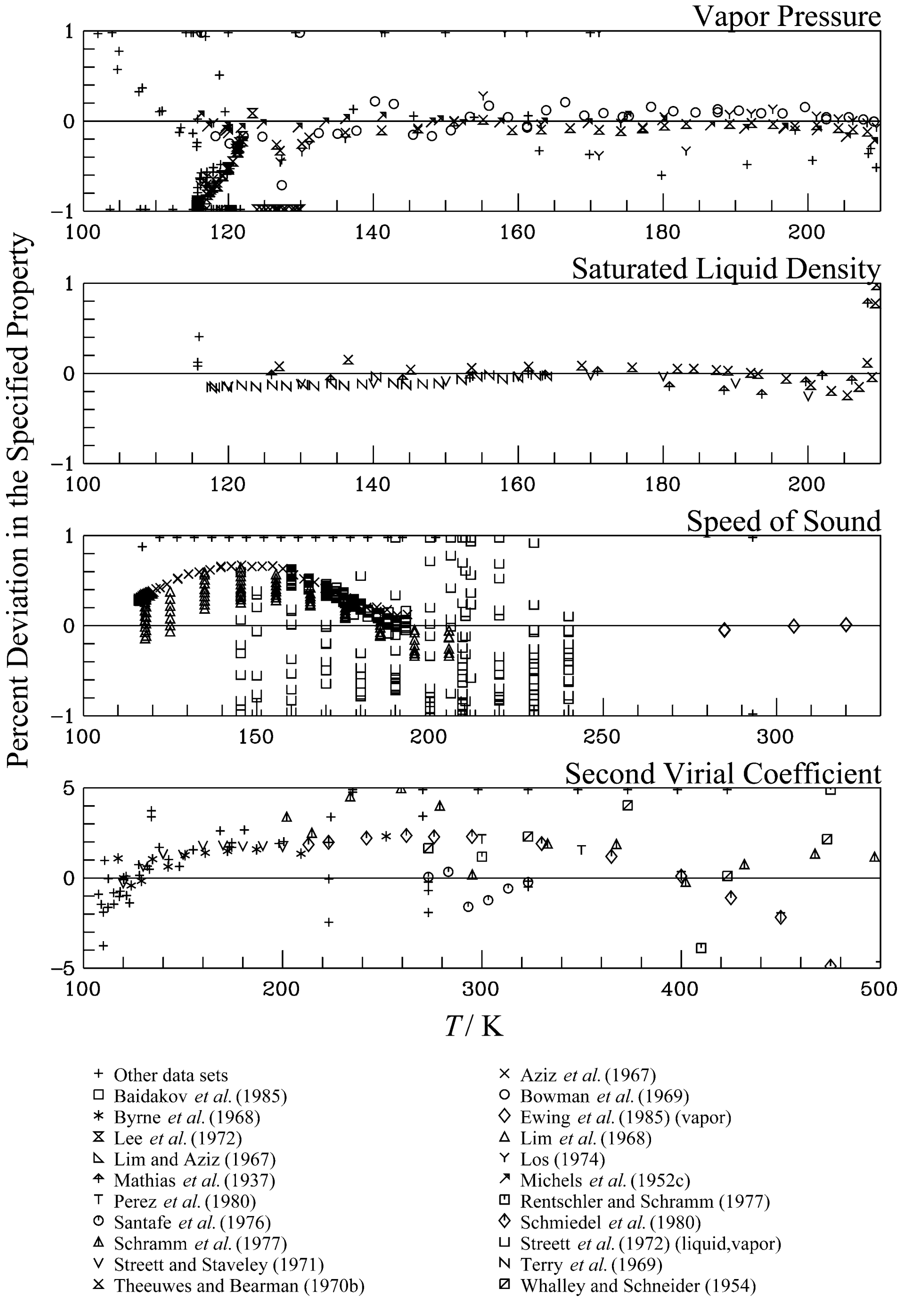

Figure 18. Krypton: comparisons of vapor pressures, saturated liquid densities, speeds of sound, and second virial coefficients calculated with the equation of state to experimental data.

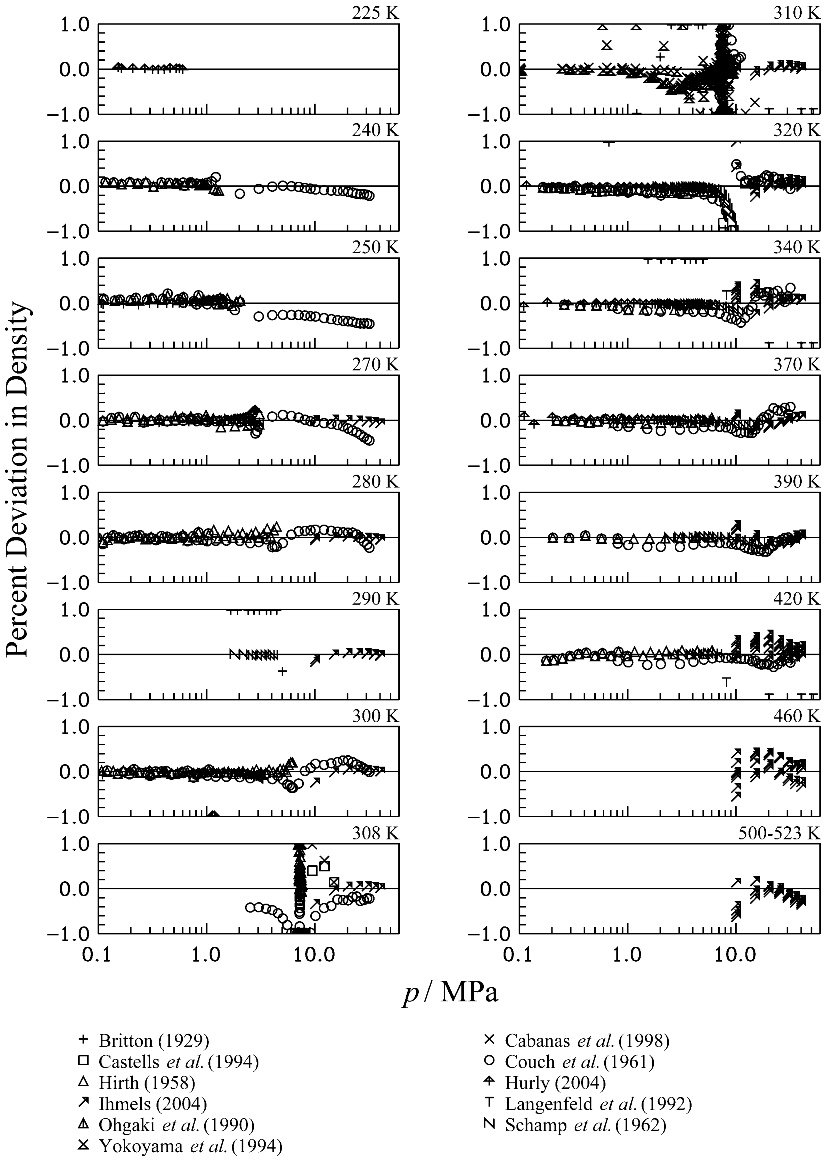

Figure 19. Nitrous oxide: comparisons of densities calculated with the equation of state to experimental data.

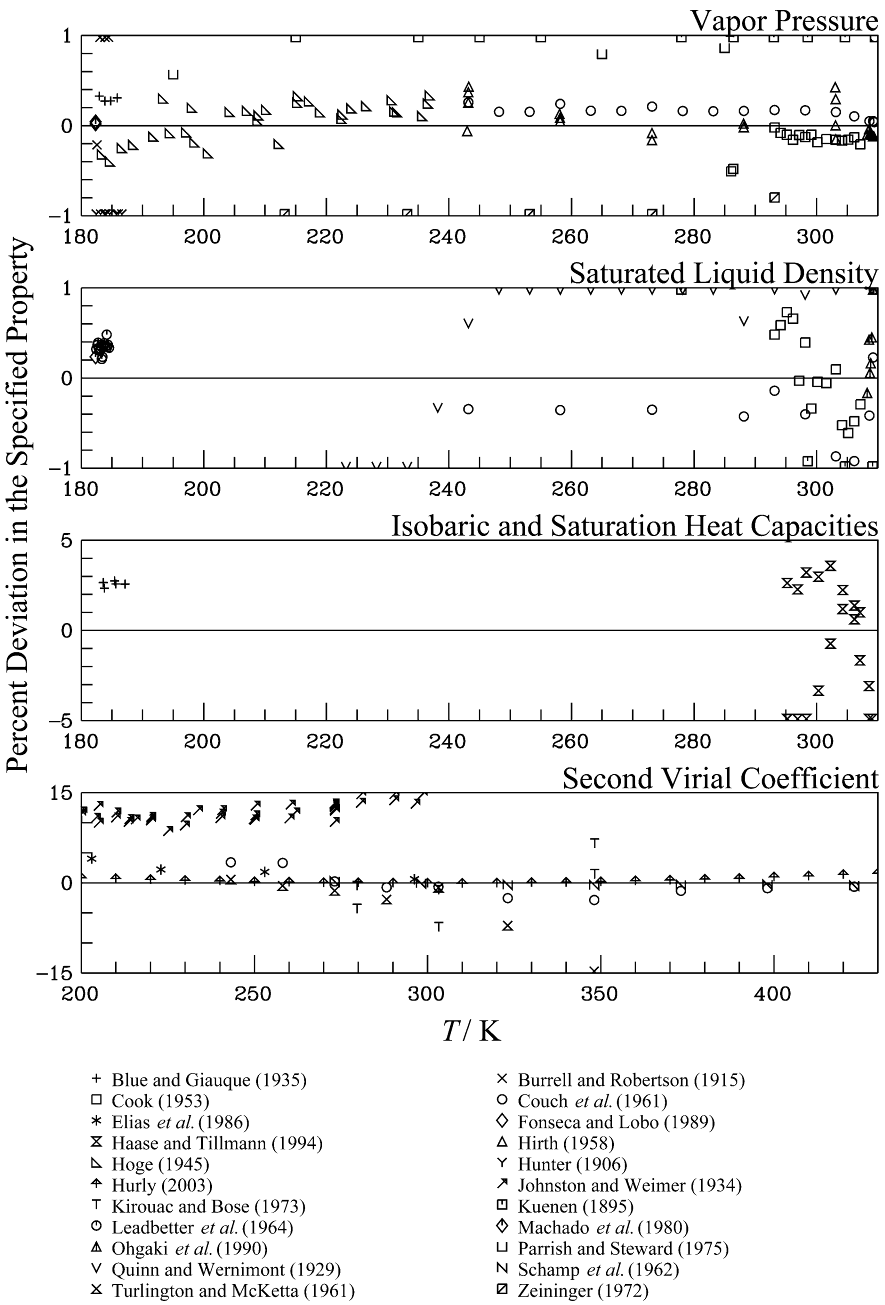

Figure 20. Nitrous oxide: comparisons of vapor pressures, saturated liquid densities, heat capacities, and second virial coefficients calculated with the equation of state to experimental data.

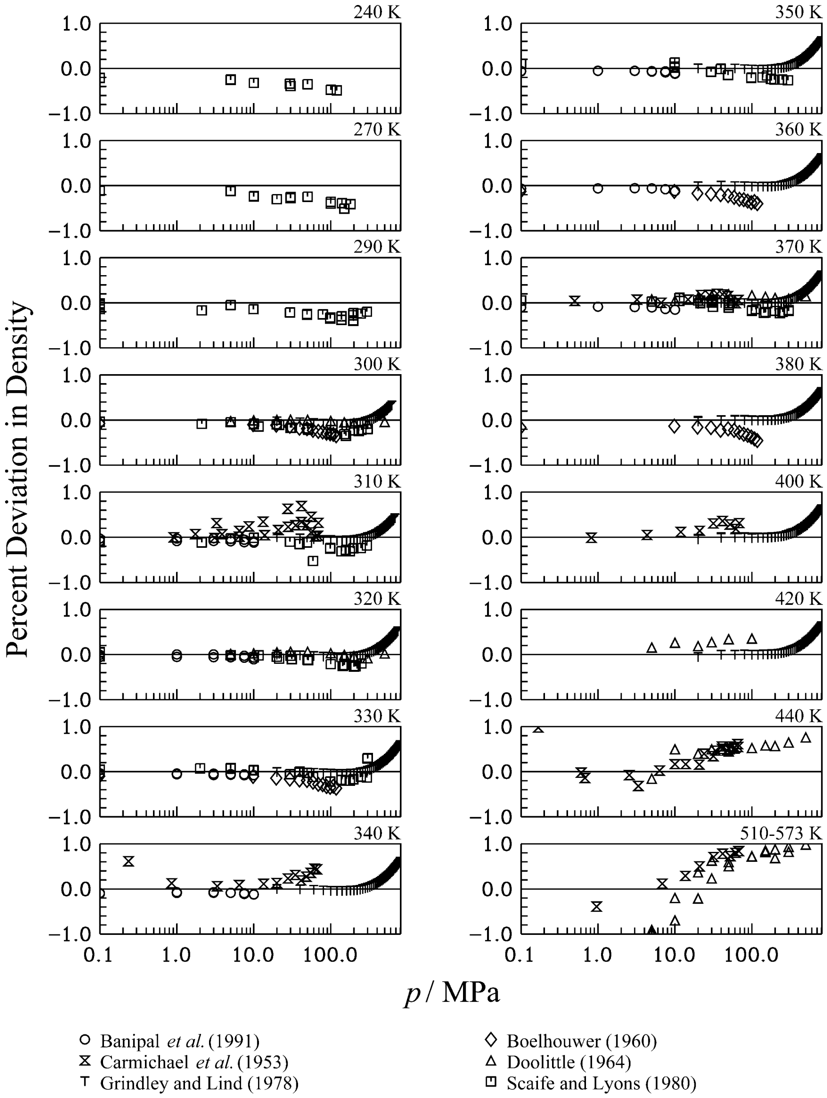

Figure 21. Nonane: comparisons of densities calculated with the equation of state to experimental data.

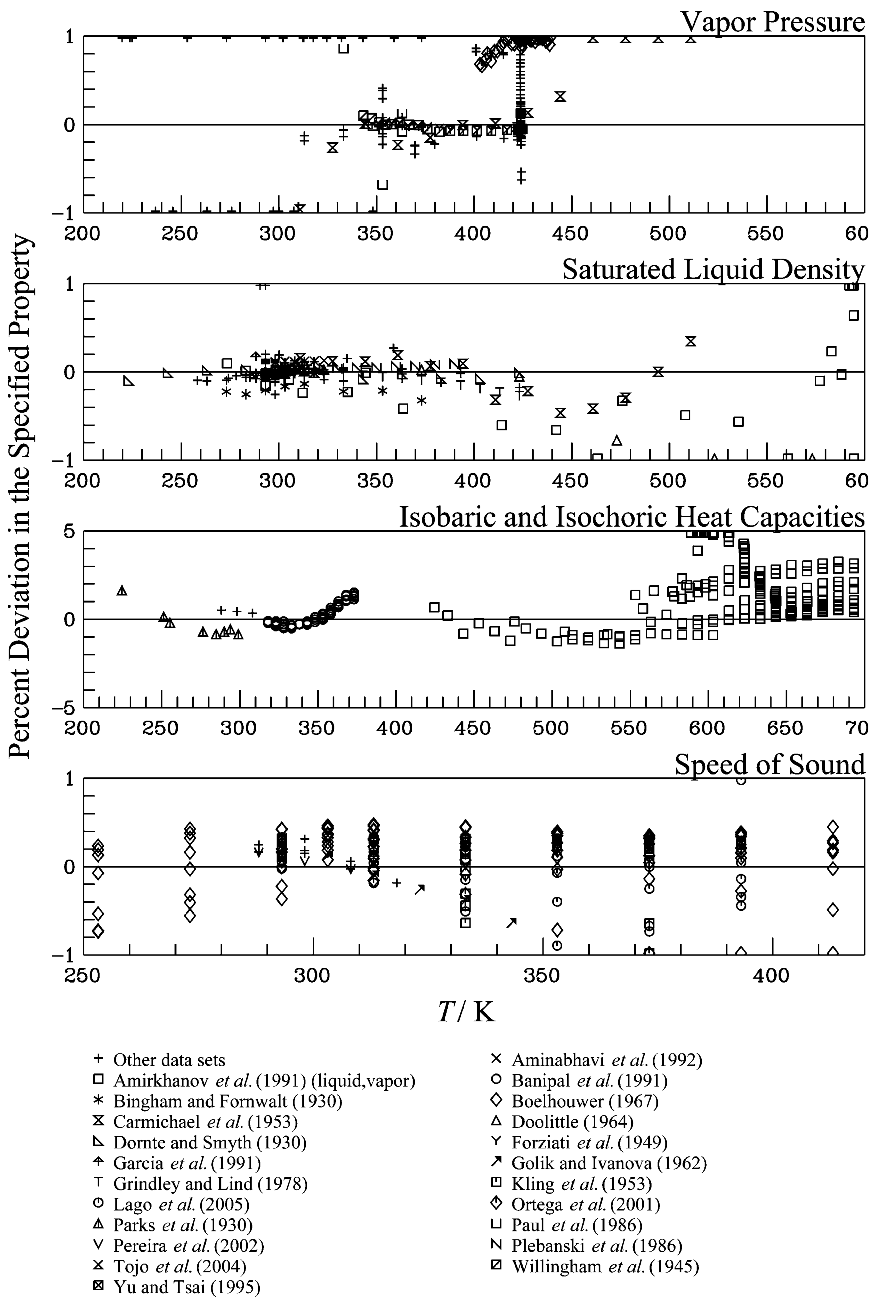

Figure 22. Nonane: comparisons of vapor pressures, saturated liquid densities, heat capacities, and speeds of sound calculated with the equation of state to experimental data.

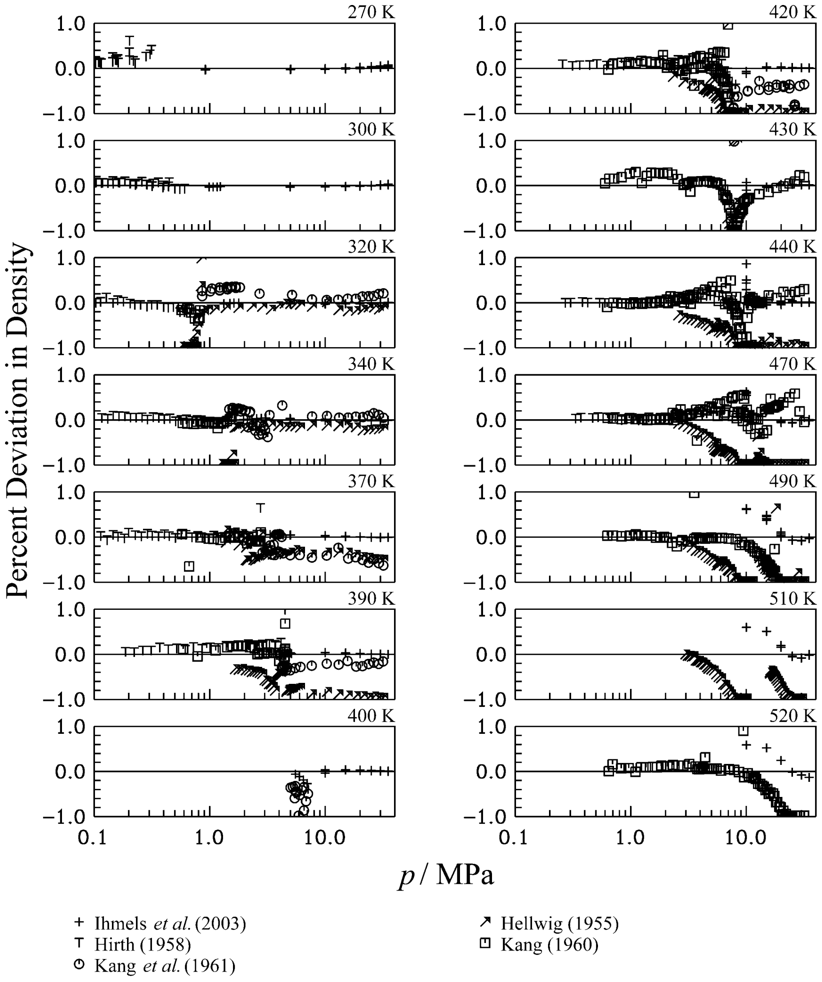

Figure 23. Sulfur dioxide: comparisons of densities calculated with the equation of state to experimental data.

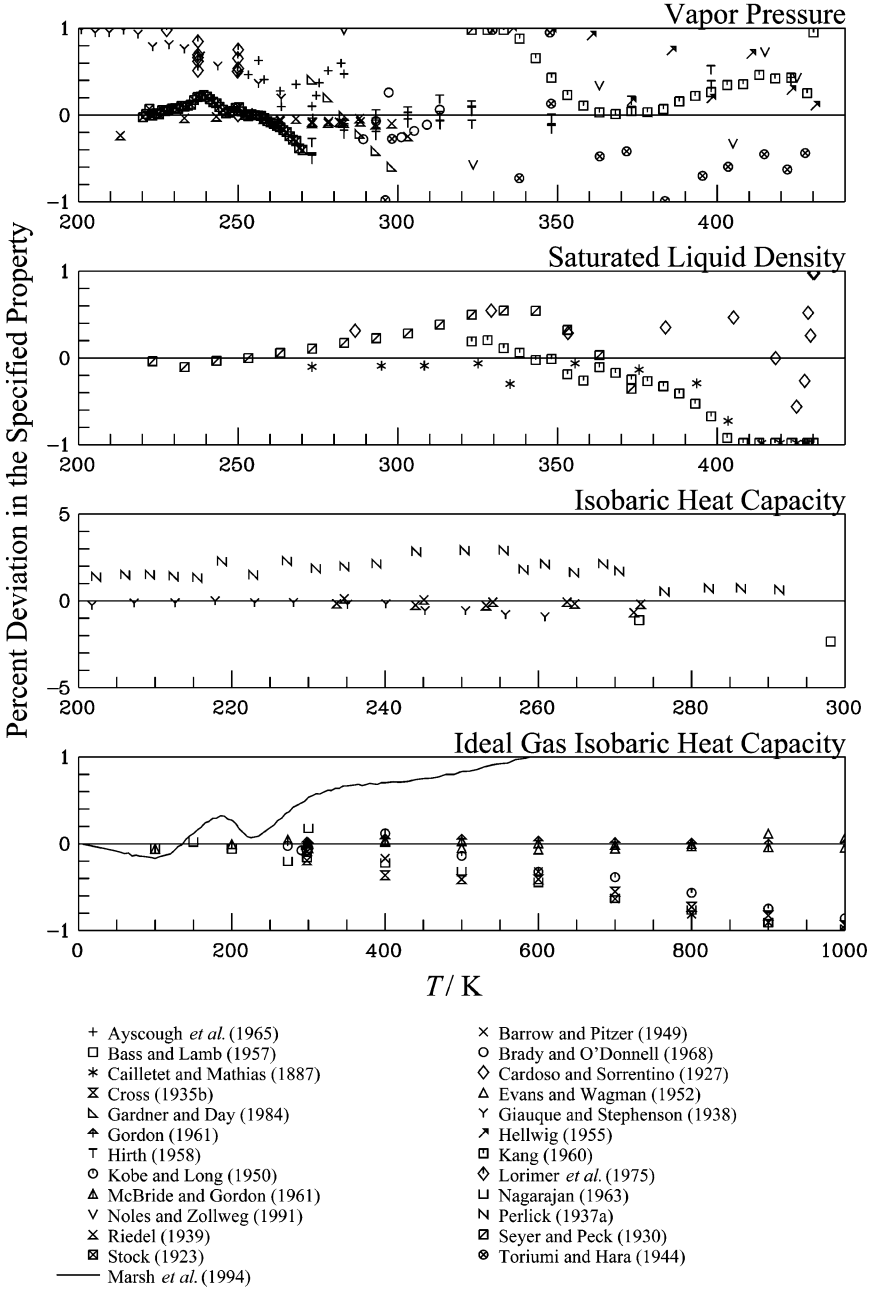

Figure 24. Sulfur dioxide: comparisons of vapor pressures, saturated liquid densities, and isobaric heat capacities calculated with the equation of state to experimental data.

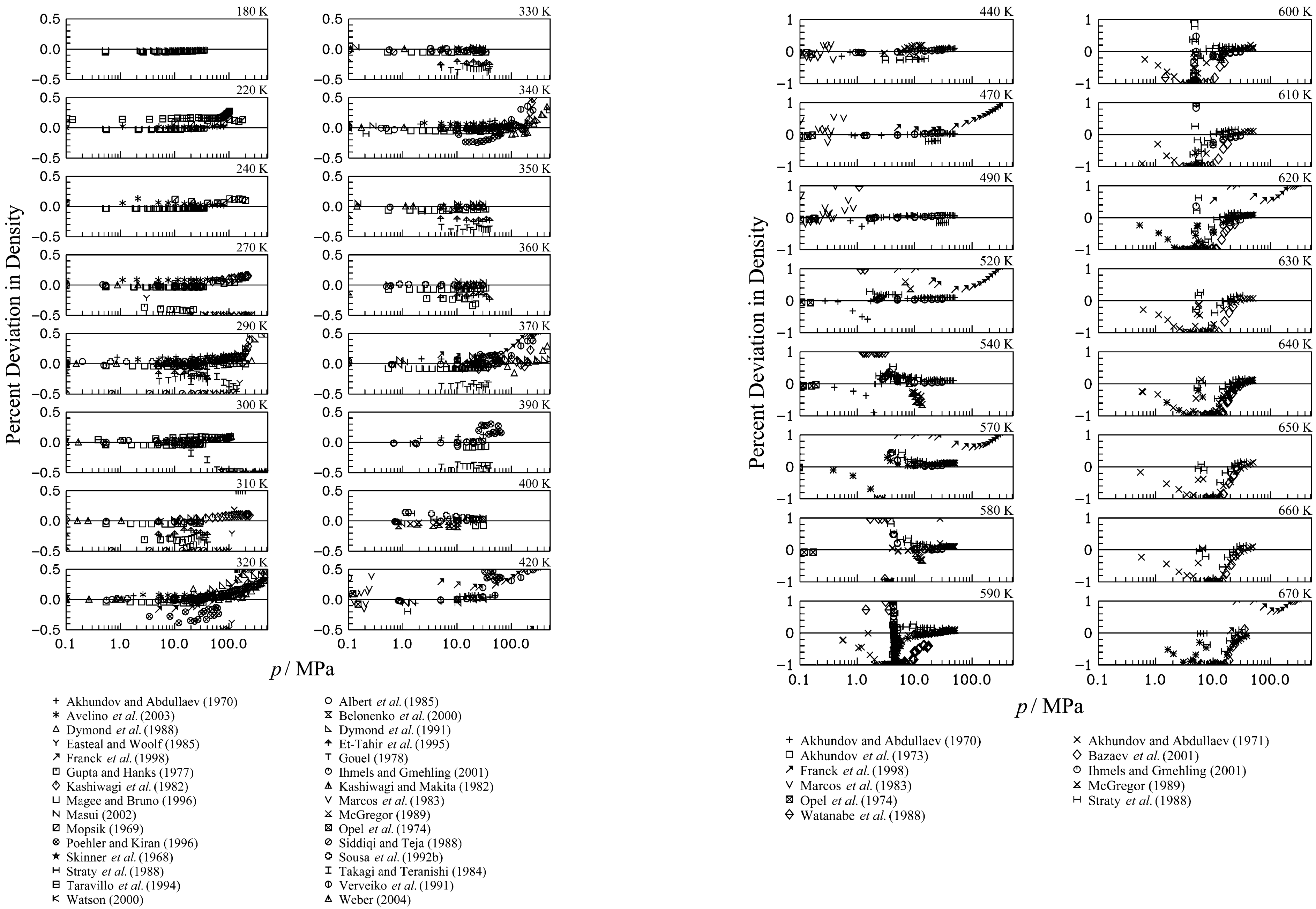

Figure 25. Toluene: comparisons of densities calculated with the equation of state to experimental data.

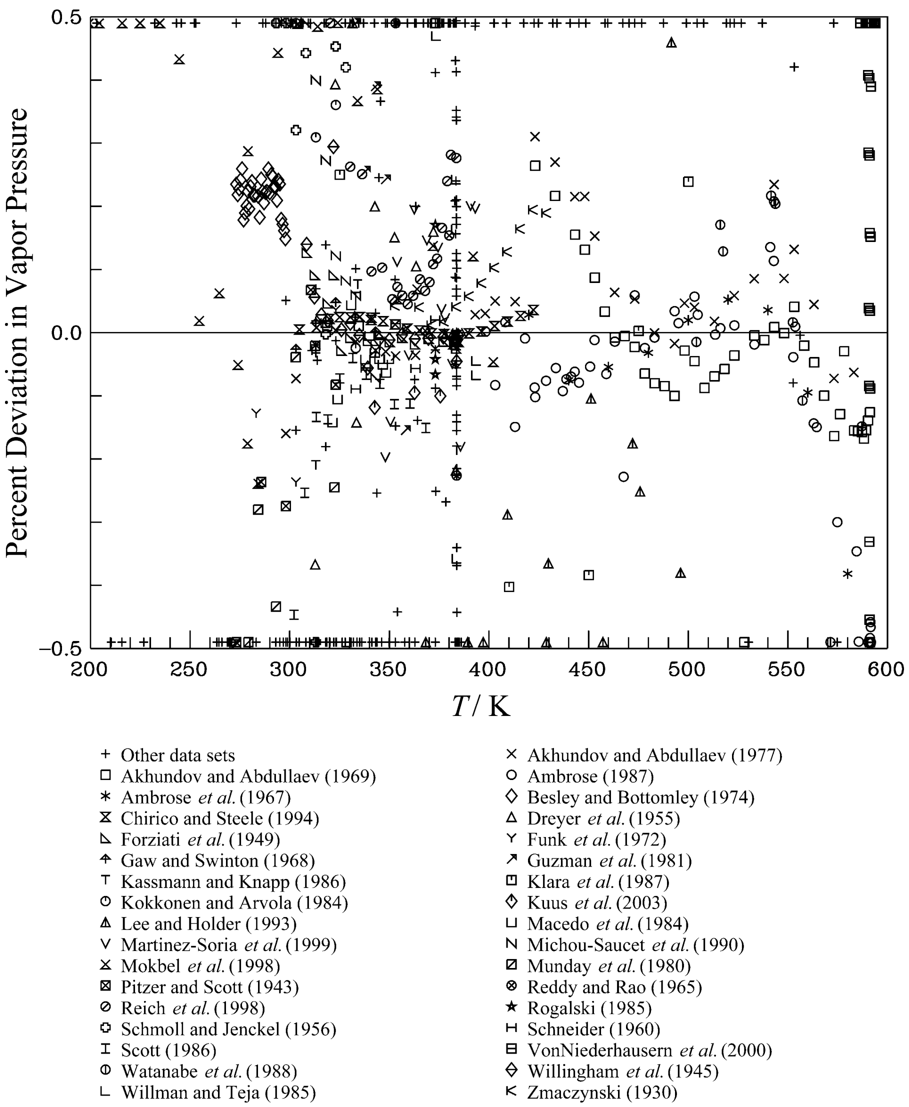

Figure 26. Toluene: comparisons of vapor pressures calculated with the equation of state to experimental data.

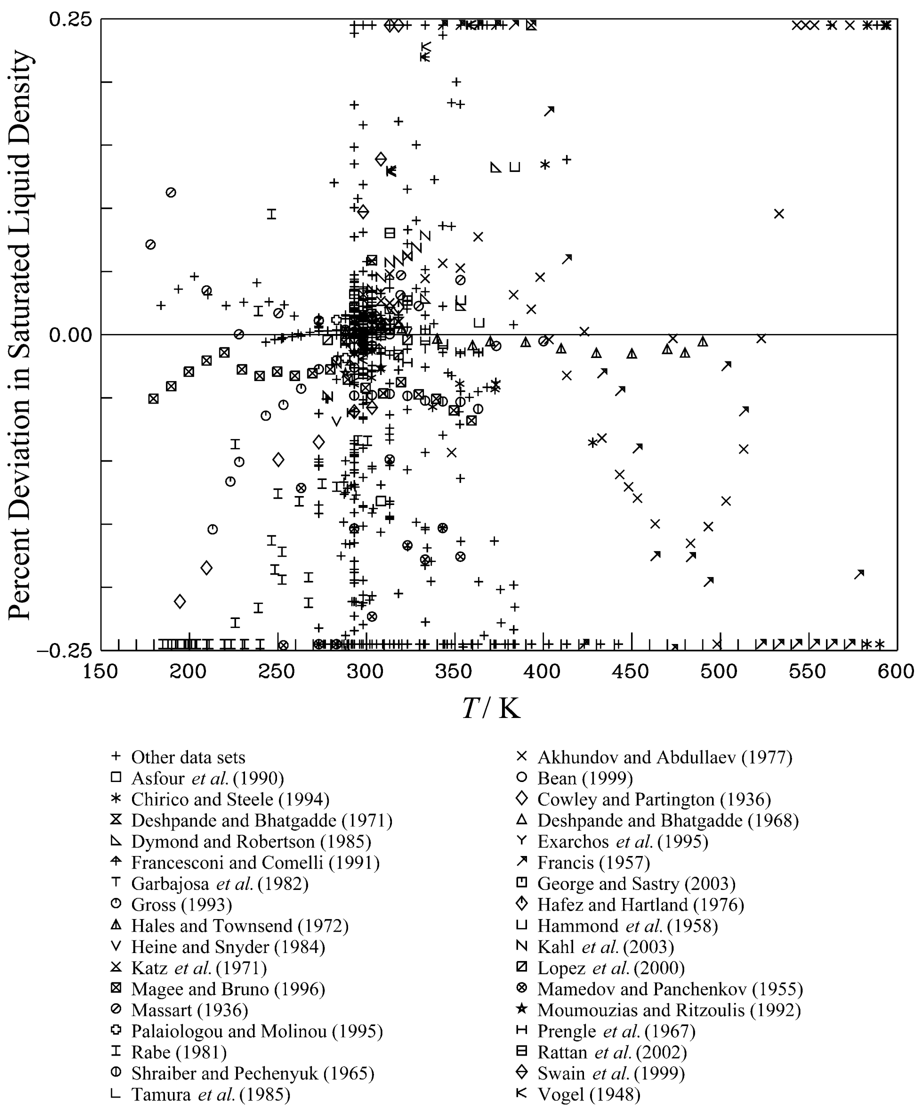

Figure 27. Toluene: comparisons of saturated liquid densities calculated with the equation of state to experimental data.

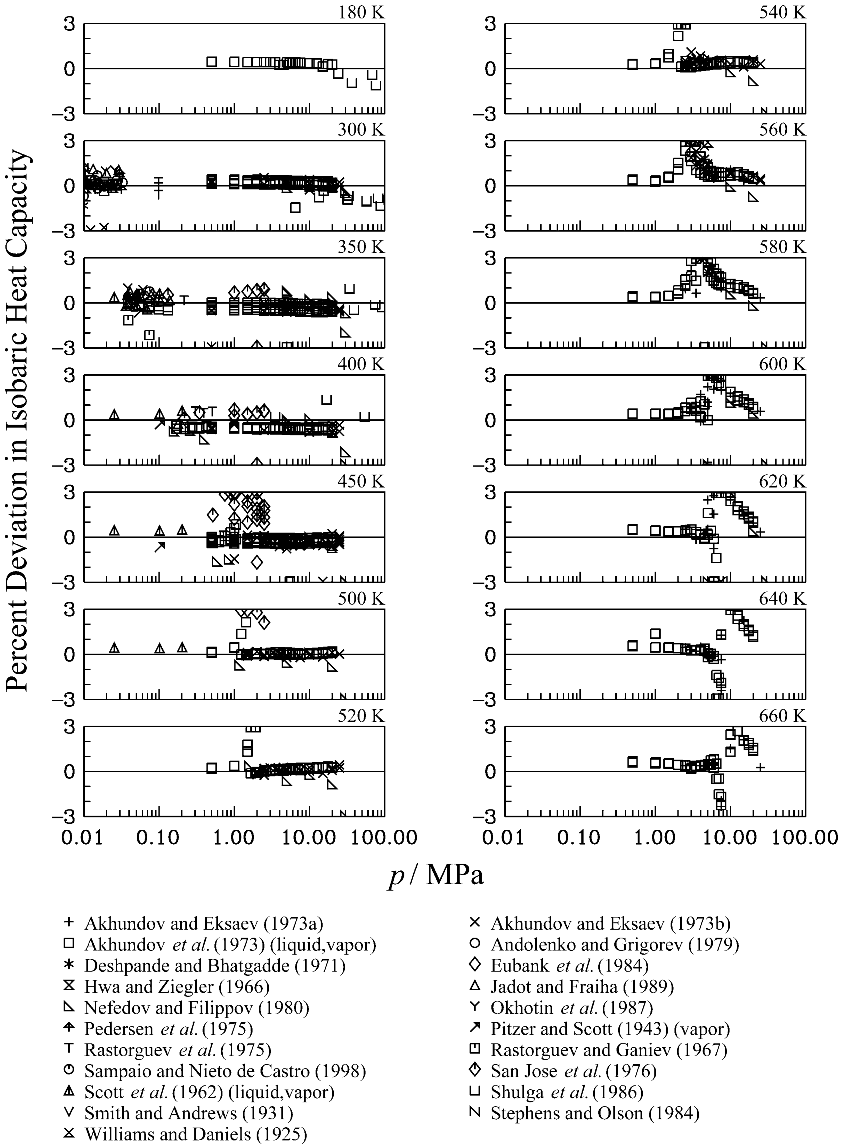

Figure 28. Toluene: comparisons of isobaric heat capacities calculated with the equation of state to experimental data.

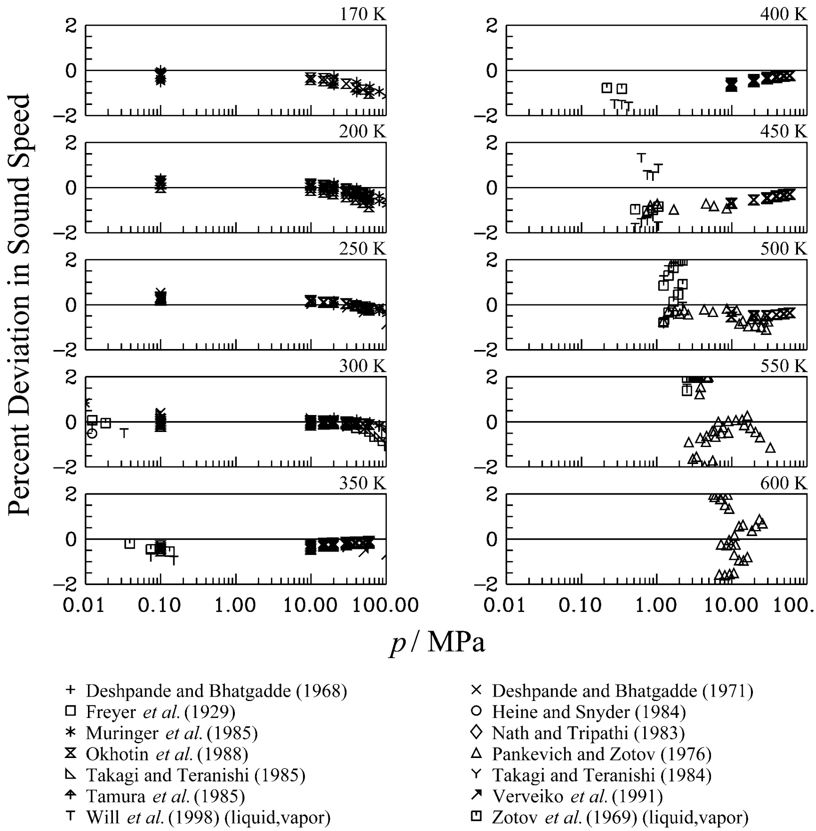

Figure 29. Toluene: comparisons of speeds of sound calculated with the equation of state to experimental data.

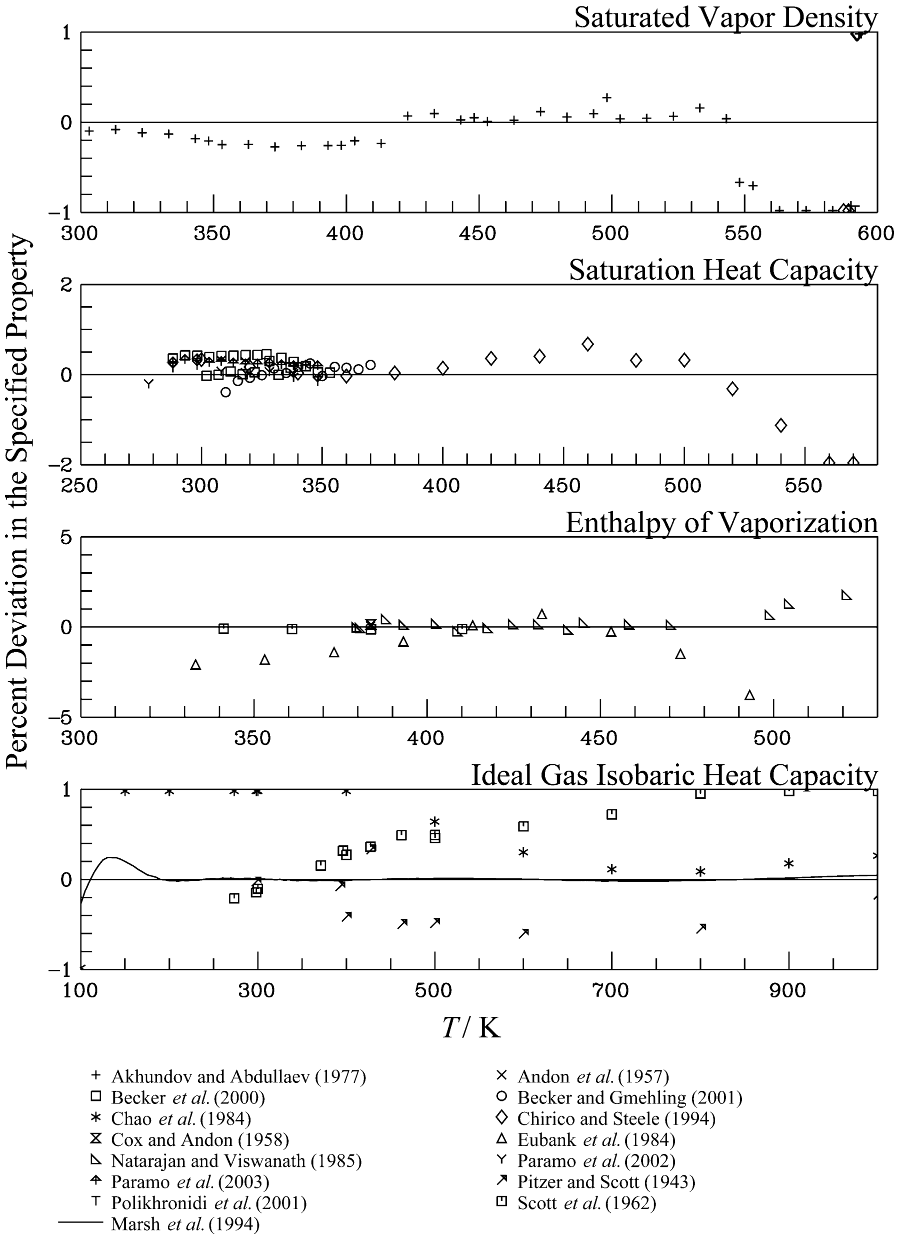

Figure 30. Toluene: comparisons of saturated vapor densities, heat capacities, and enthalpies of vaporization calculated with the equation of state to experimental data.

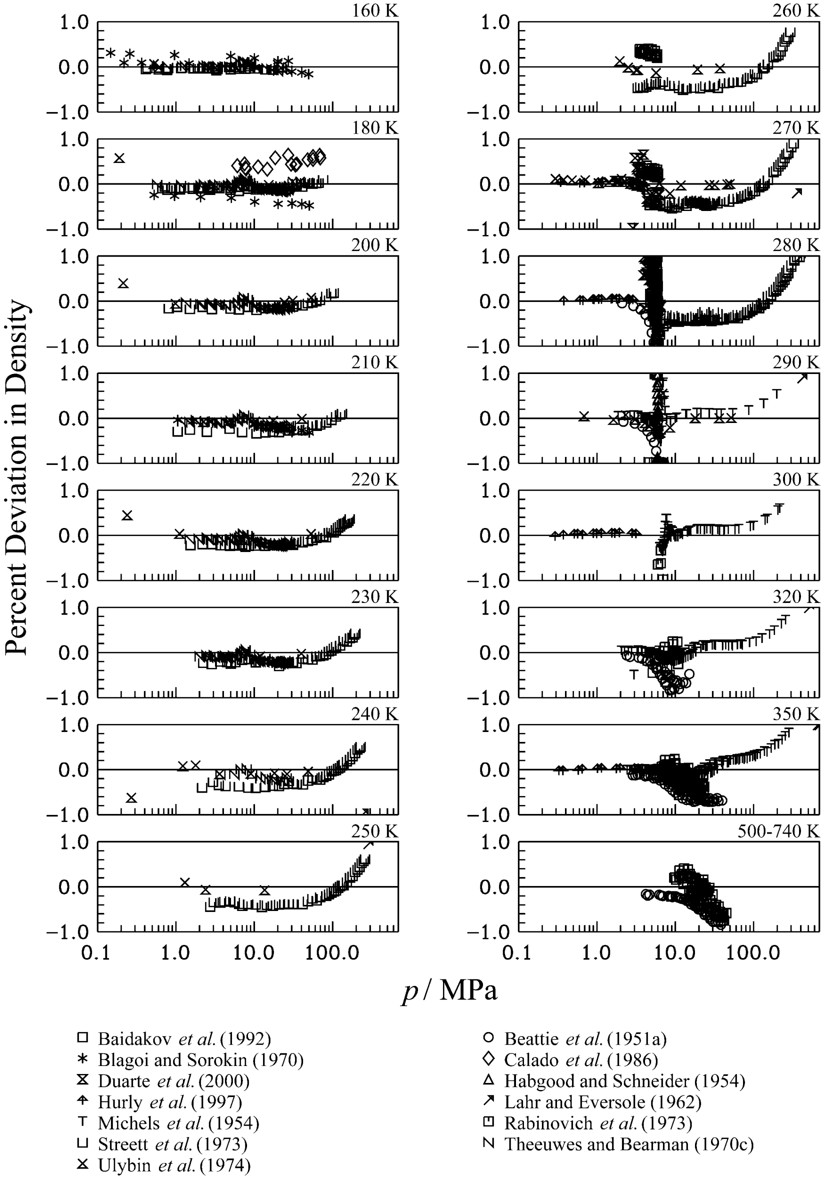

Figure 31. Xenon: comparisons of densities calculated with the equation of state to experimental data.

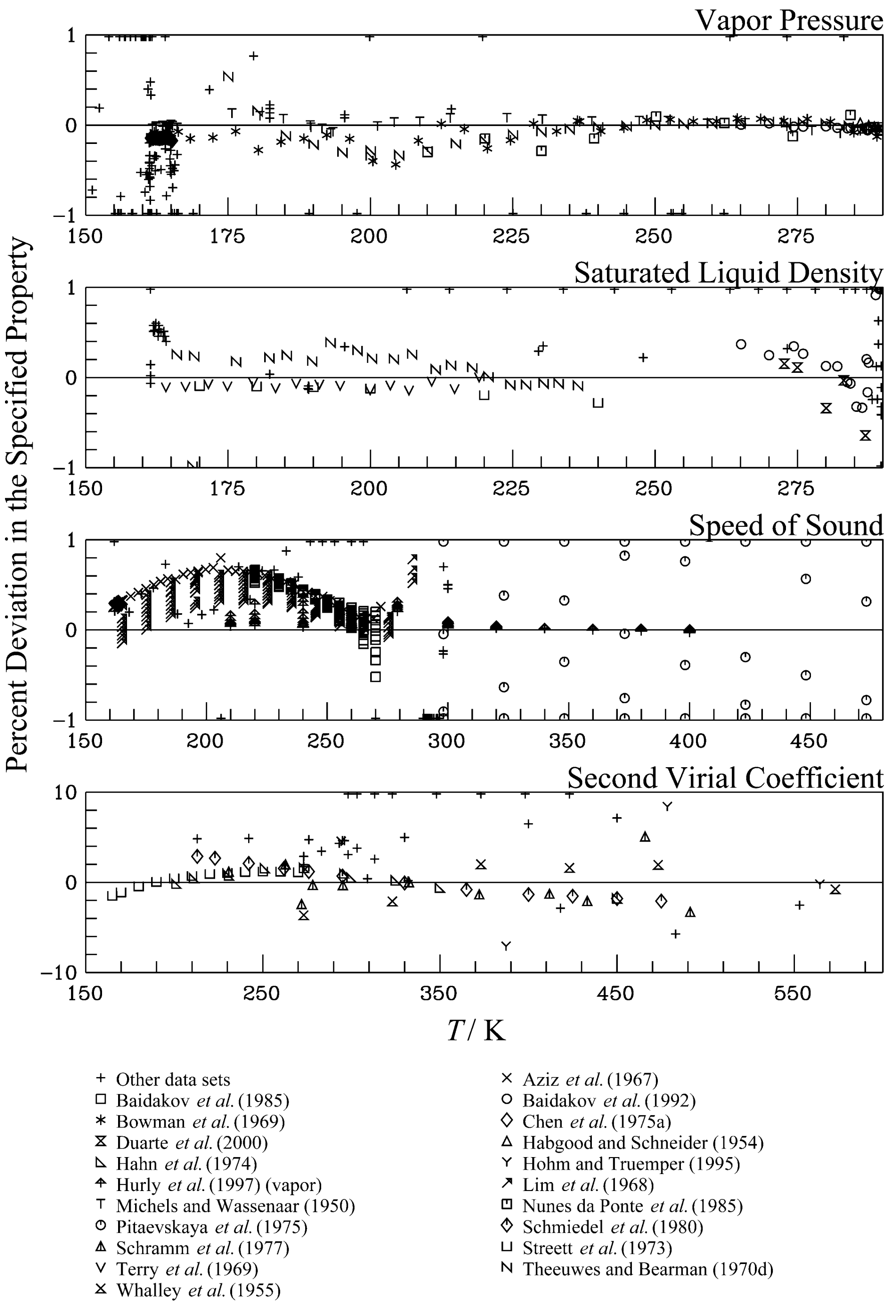

Figure 32. Xenon: comparisons of vapor pressures, saturated liquid densities, speeds of sound, and second virial coefficients calculated with the equation of state to experimental data.

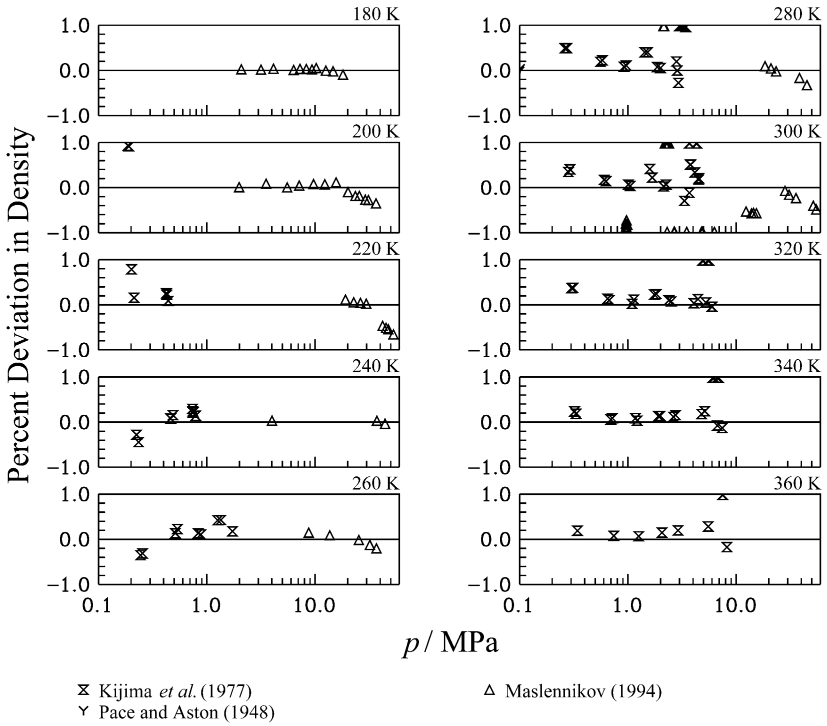

Figure 33. Hexafluoroethane (R-116): comparisons of densities calculated with the equation of state to experimental data.

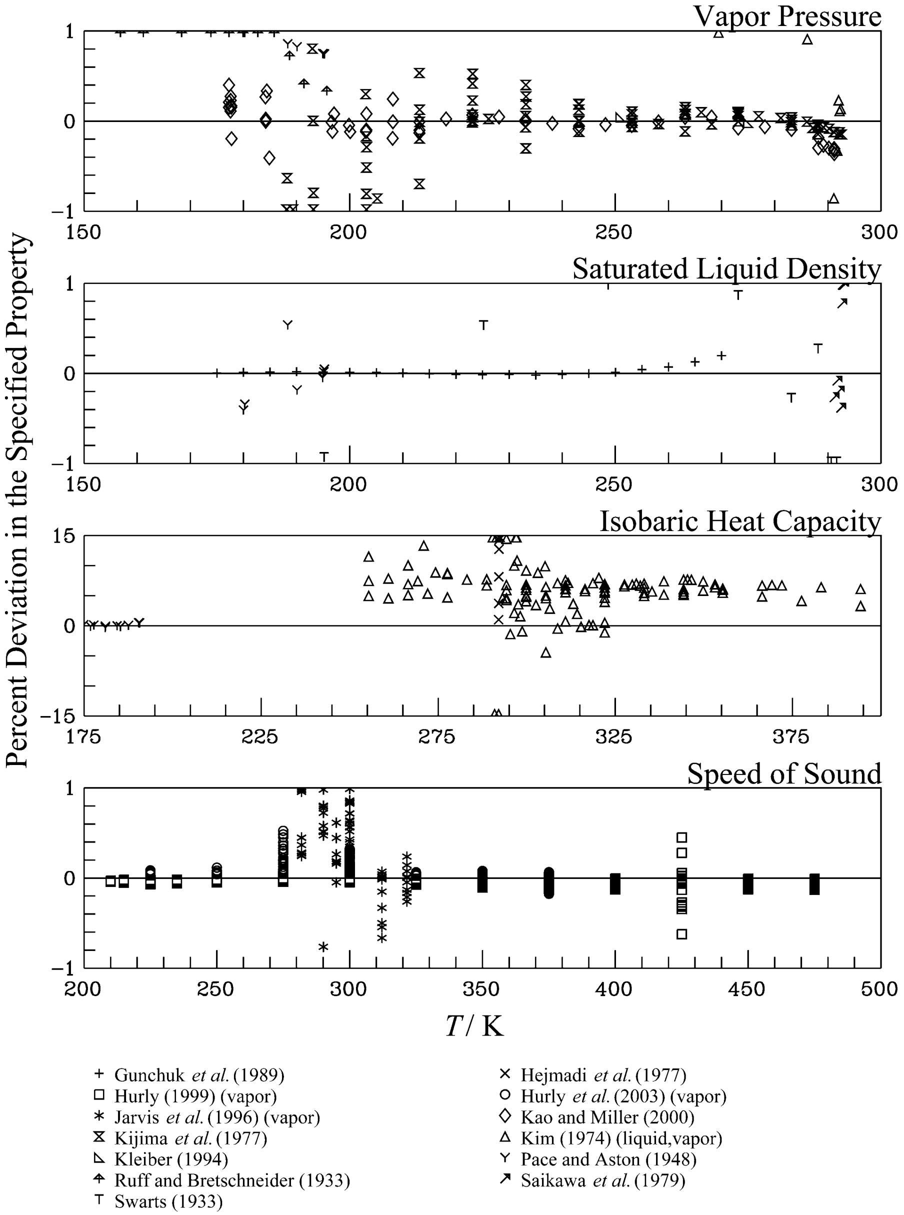

Figure 34. Hexafluoroethane (R-116): comparisons of vapor pressures, saturated liquid densities, isobaric heat capacities, and speeds of sound calculated with the equation of state to experimental data.

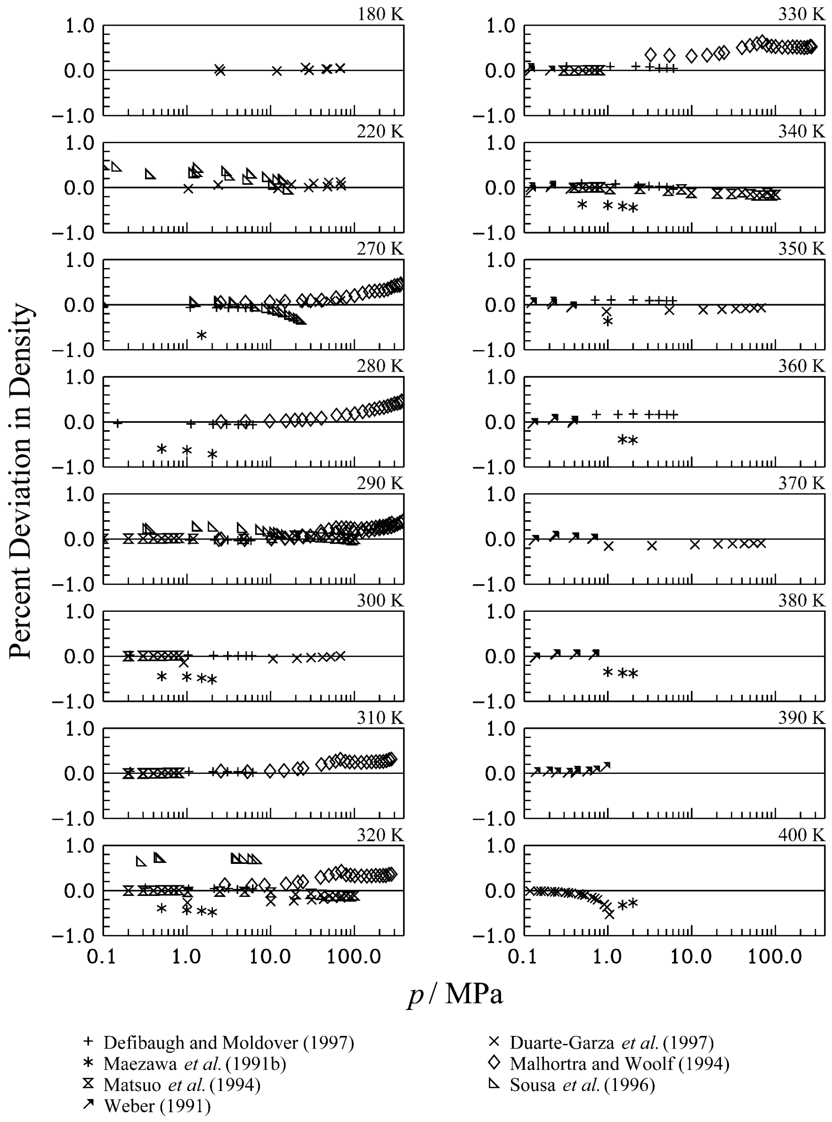

Figure 35. 1,1-Dichloro-1-fluoroethane (R-141b): comparisons of densities calculated with the equation of state to experimental data.

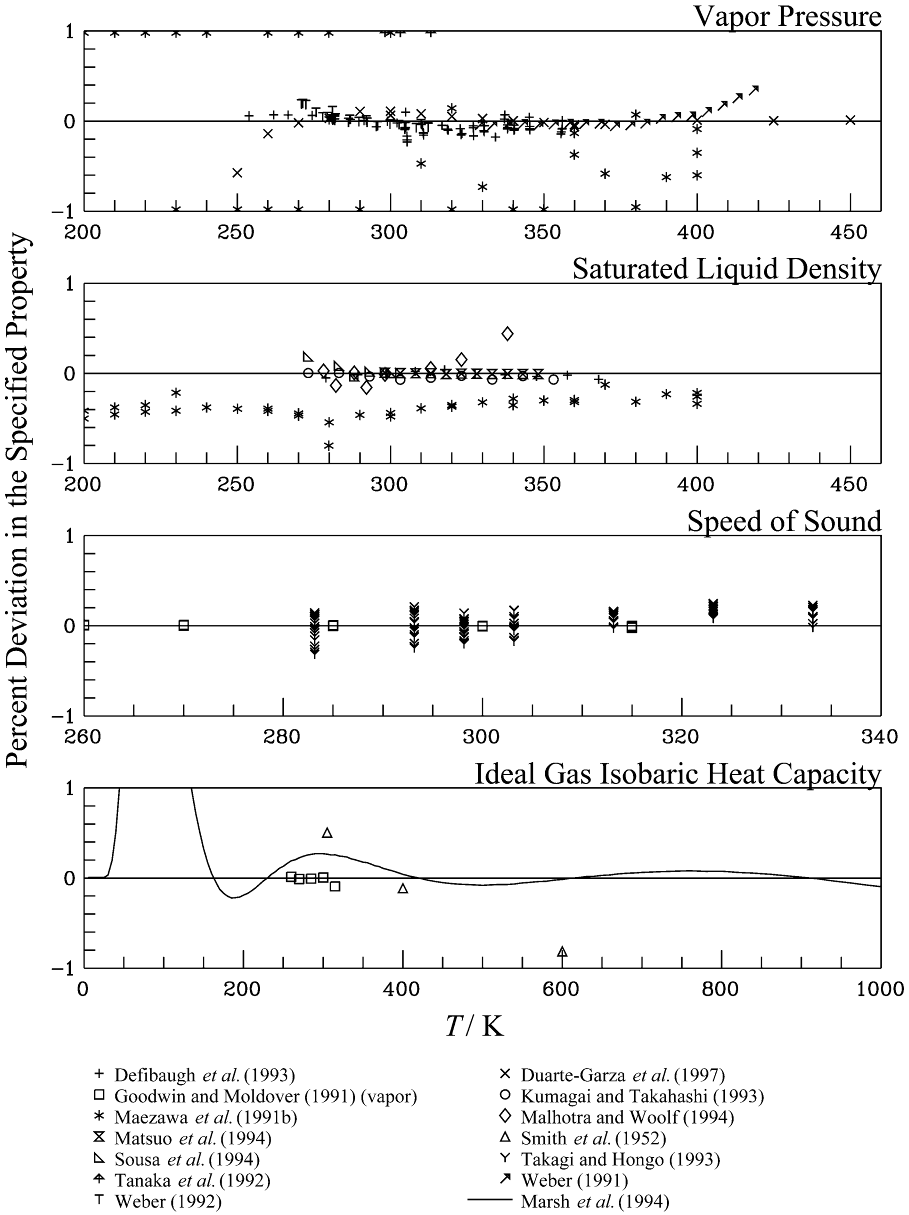

Figure 36. 1,1-Dichloro-1-fluoroethane (R-141b): comparisons of vapor pressures, saturated liquid densities, isobaric heat capacities, and speeds of sound calculated with the equation of state to experimental data.

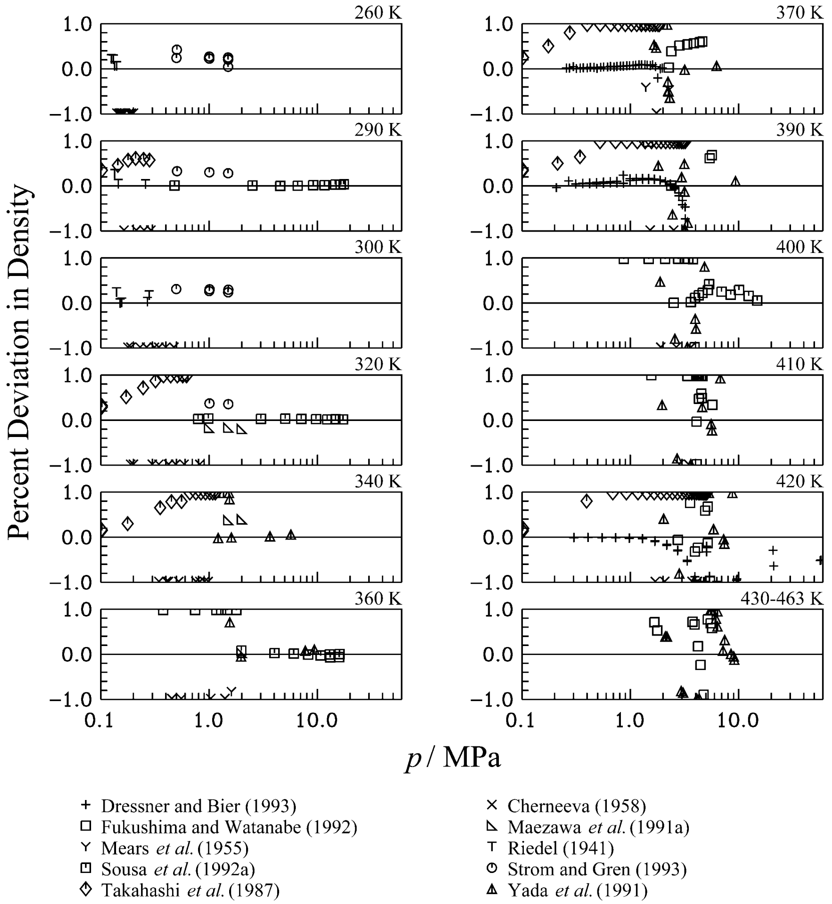

Figure 37. 1-Chloro-1,1-difluoroethane (R-142b): comparisons of densities calculated with the equation of state to experimental data.

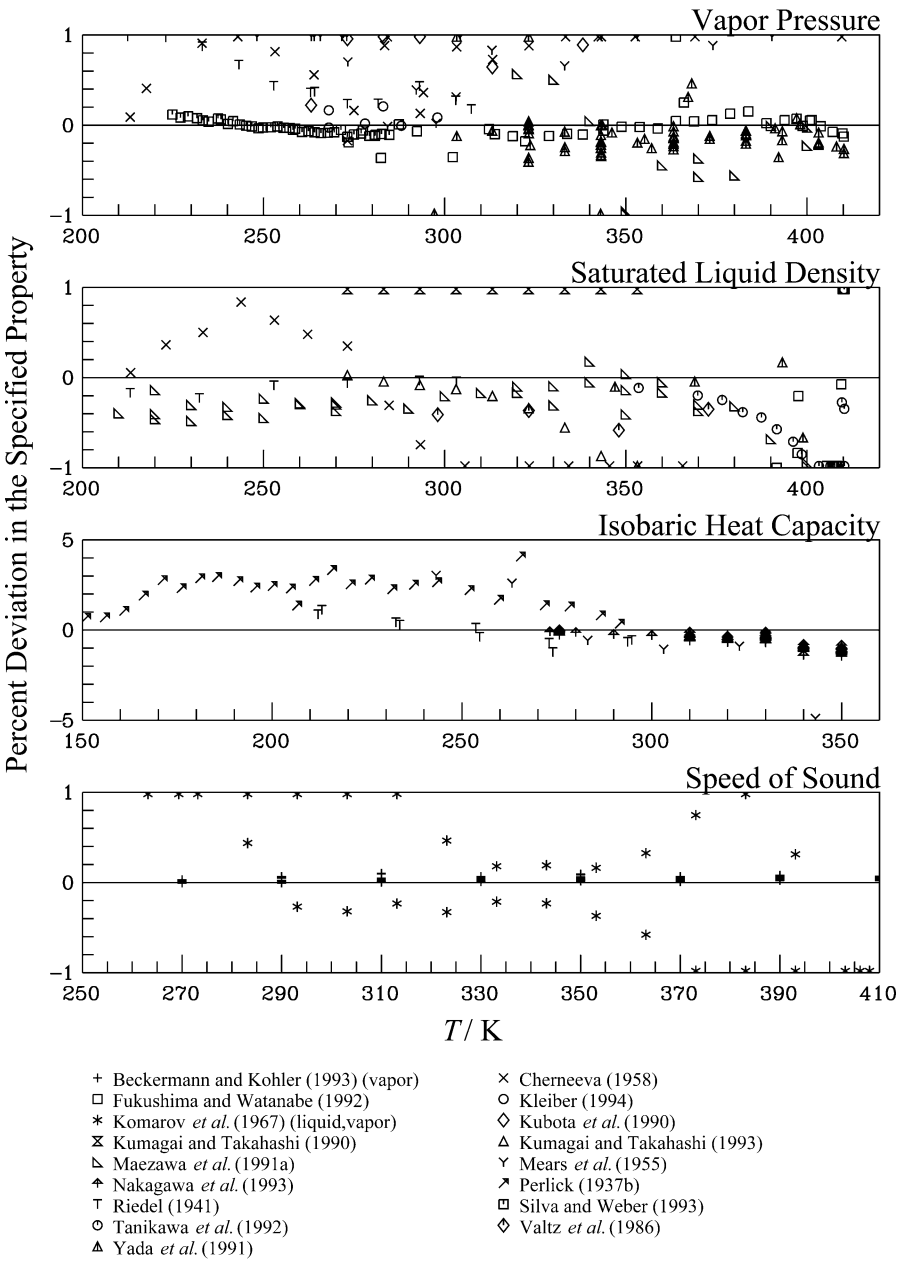

Figure 38. 1-Chloro-1,1-difluoroethane (R-142b): comparisons of vapor pressures, saturated liquid densities, isobaric heat capacities, and speeds of sound calculated with the equation of state to experimental data.

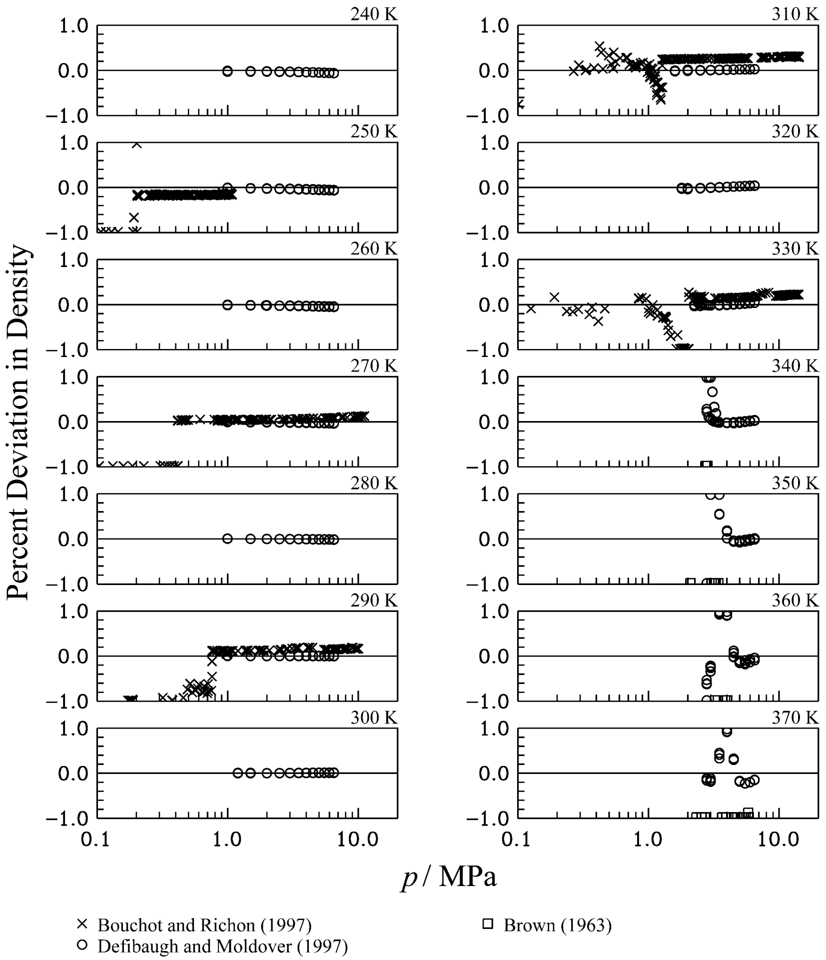

Figure 39. Octafluoropropane (R-218): comparisons of densities calculated with the equation of state to experimental data.

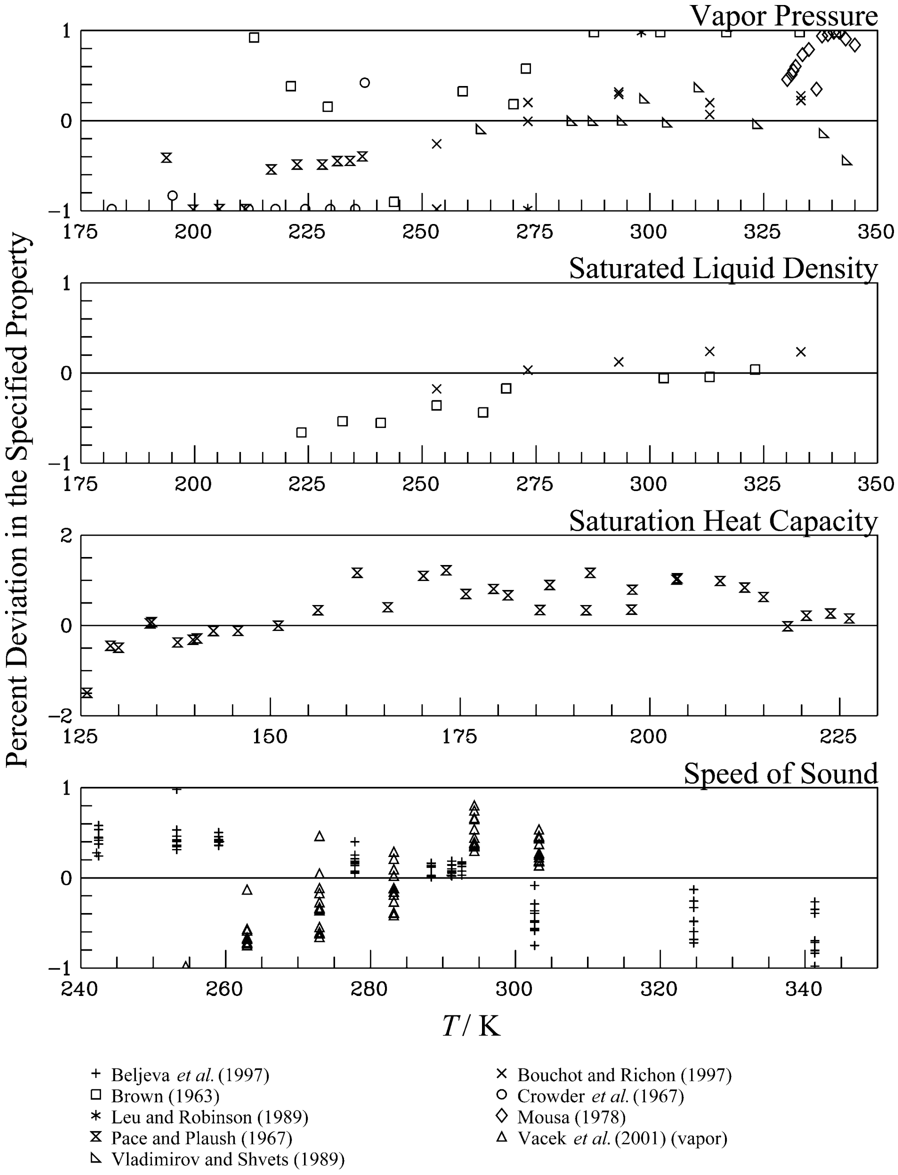

Figure 40. Octafluoropropane (R-218): comparisons of vapor pressures, saturated liquid densities, saturation heat capacities, and speeds of sound calculated with the equation of state to experimental data.

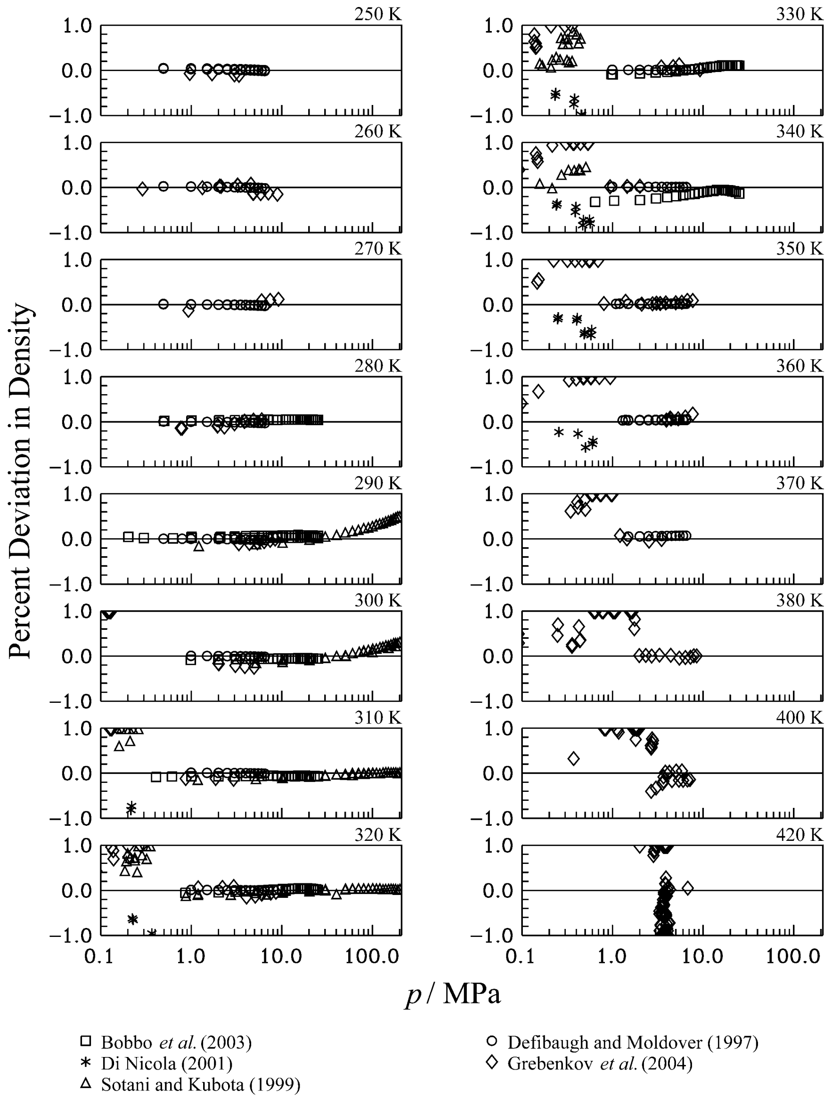

Figure 41. 1,1,1,3,3-Pentafluoropropane (R-245fa): comparisons of densities calculated with the equation of state to experimental data.

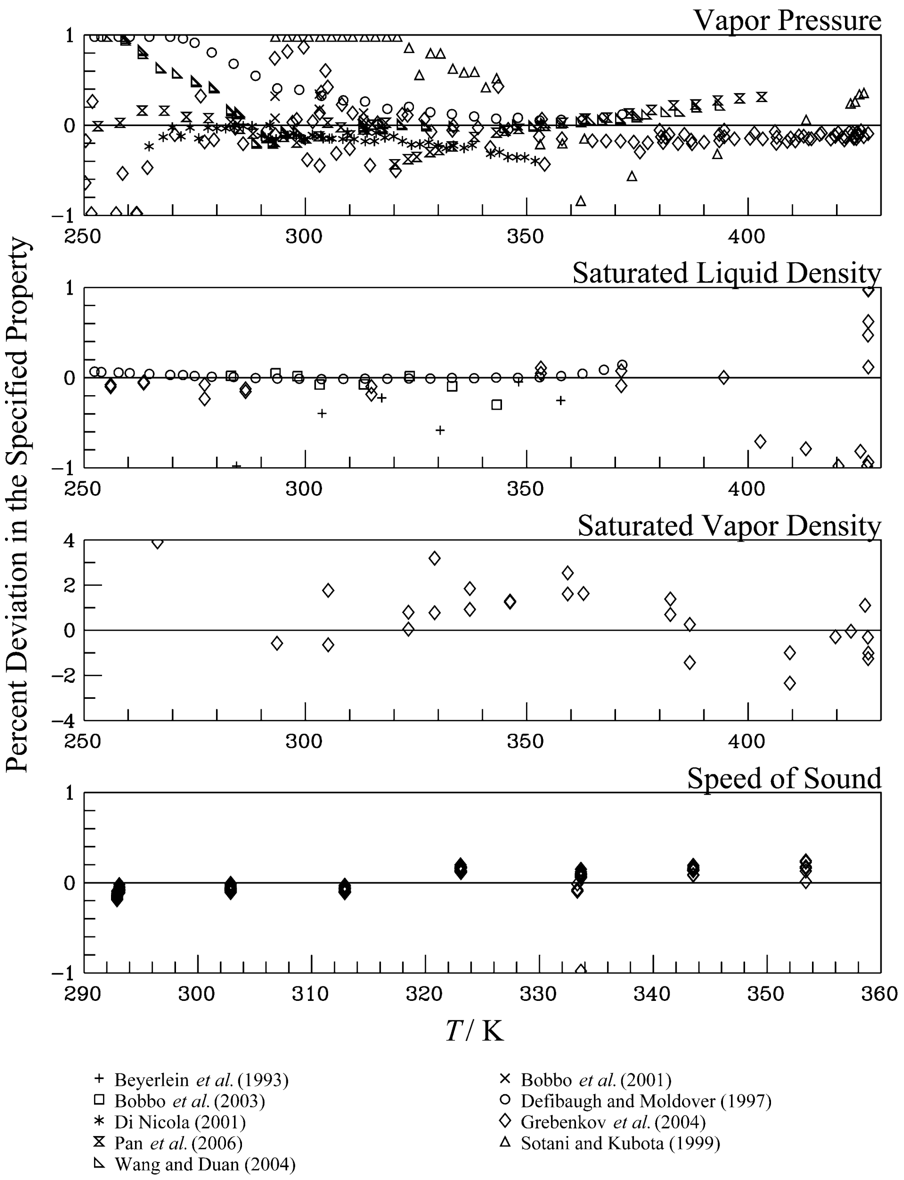

Figure 42. 1,1,1,3,3-Pentafluoropropane (R-245fa): comparisons of vapor pressures, saturated liquid and vapor densities, and speeds of sound calculated with the equation of state to experimental data.

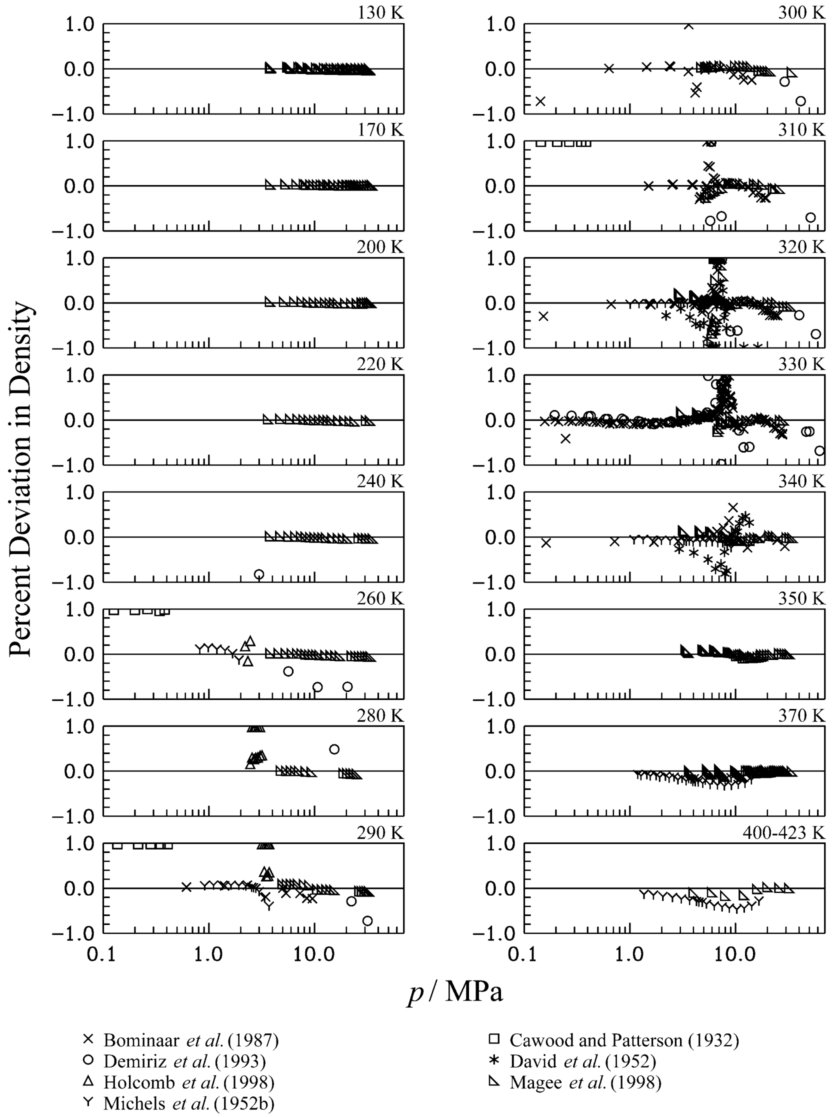

Figure 43. Fluoromethane (R-41): comparisons of densities calculated with the equation of state to experimental data.

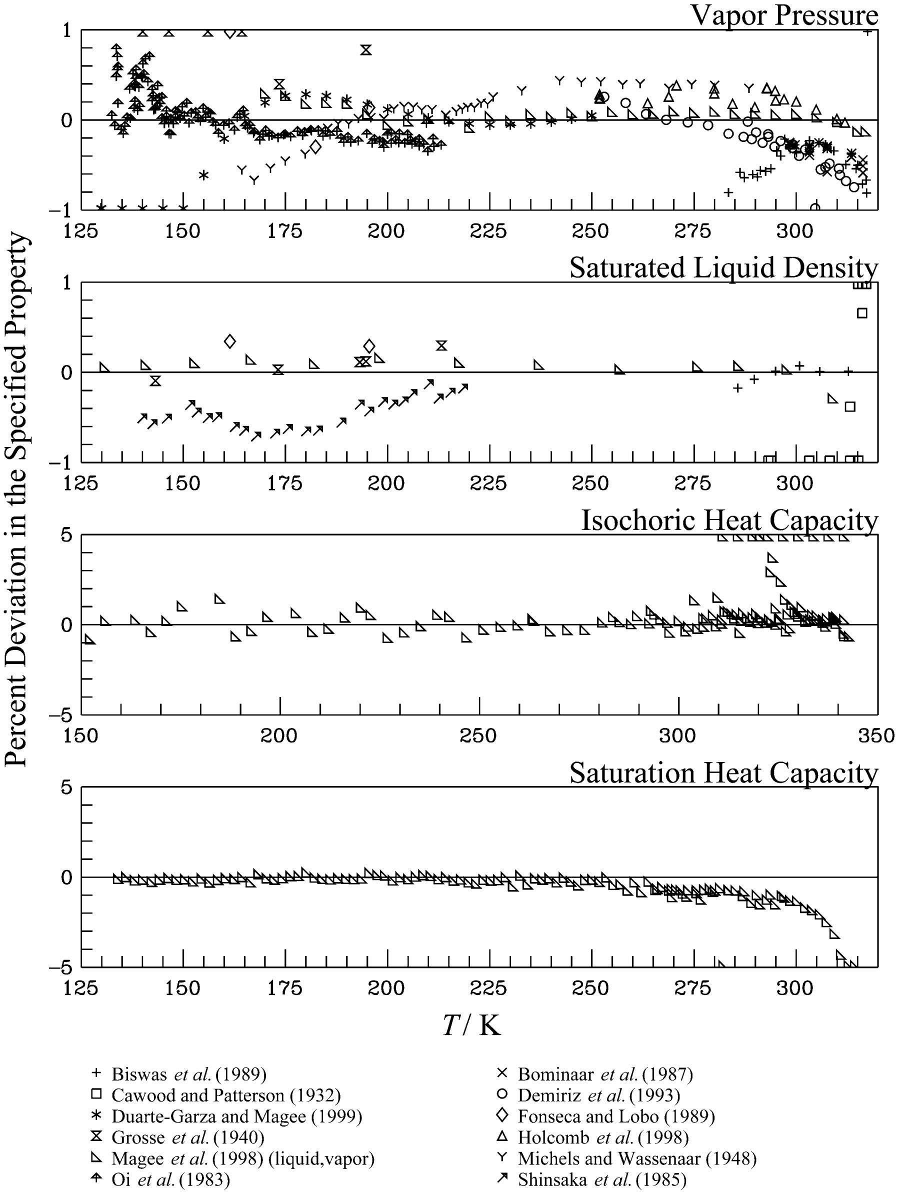

Figure 44. Fluoromethane (R-41): comparisons of vapor pressures, saturated liquid densities, and heat capacities calculated with the equation of state to experimental data.

of Michels et al. (1952d) were used as primary data. However, the equation shows a slight systematic offset from the vapor pressure measurements of Michels et al. There are only a few measurements on the liquid-phase isobaric heat capacity of carbon monoxide (all of which lie below 86 K), and the scatter in the available data is about 2 %. On the other hand, there are a substantial number of second virial coefficients, with agreement of about (5 to 10) % for most of the data points including the values of Connolly (1964), McElroy and Buchanan (1995), and Michels et al. (1952a).

The equation of state is valid from the triple point to 500 K with pressures to 100 MPa. At higher pressures, the deviations from the equation increase rapidly and the equation should not be used above 100 MPa. The uncertainties in the equation are 0.3 % in density (approaching 1 % near the critical point), 0.2 % in vapor pressure, and 2 % in heat capacities. The uncertainty in the speed of sound is unknown.

Carbonyl Sulfide. Experimental measurements for carbonyl sulfide and their deviations from the equation of state are summarized in Table 9 and shown in Figures 5 and 6. Aside from the recent $p\rho T$ measurements of Ihmels and Gmehling (2001), the data situation for carbonyl sulfide is quite poor. The limited data that do exist quite often disagree with other data sets. Fortunately, the data of Ihmels and Gmehling span the temperature range from (273 to 623) K with pressures up to 40 MPa and have formed much of the basis for the new equation. Both the nonpolar and polar forms were applied to carbonyl sulfide, but with only limited success. It was not possible to represent all of the experimental $p\rho T$ data to within 1 % in density with either form at high temperatures while maintaining accurate calculations at lower temperatures. The nonpolar form of the equation was slightly better and was used in the final fit. Below 450 K, nearly all of the deviations of the equation from the data of Ihmels and Gmehling are within 0.1 % in density, except for the measurements at 10 MPa at high temperatures, which show a maximum error of 0.5 % at 418 K. Above 450 K, the deviations start to increase and reach a maximum of 1 % at 500 K and a maximum of 3 % at 600 K.

There are several data sets for the saturated liquid density. Below 270 K, the equation agrees with the data of Partington and Neville (1951) to within 0.4 %. However, increasing deviations are observed with increasing temperatures above 270 K, with some exceeding 10 % at the highest temperatures (approaching the critical point). This discrepancy is also reflected in their measured critical temperature, a value that is lower by more than 3 K than that of Robinson and Senturk (1979a). The older data of Pearson et al. (1932) also demonstrate a large deviation in the saturated liquid density from the data of Partington and Neville, as shown in Figure 6. On the basis of these comparisons and the observations of the generalized shape of the saturation dome in comparison with other fluids, these data were not used in the fit at the higher temperatures. Rather, the single-phase data of Ihmels and Gmehling were used to determine the saturation properties of the equation. The vapor-phase $p\rho T$ data of Robinson and Senturk (1979b) were included during the fitting of the equation. However, the equation was not able to represent all of the values at 383 K to within 1 % in density. Additional measurements are needed to validate the uncertainty statements at densities below the critical density and at high temperatures.

The vapor pressure measurements of Kemp and Giauque (1937) and Robinson and Senturk (1979a) appear to be inconsistent by about 1 %. However, there is a temperature difference of 40 K between the upper limit of the Kemp and Giauque data and the lower limit of the Robinson and Senturk data. Both data sets are represented to within 0.5 %. There are a limited number of isobaric heat capacity measurements between the triple point temperature and 220 K, with average deviations of about 1 %.

The resulting equation has uncertainties of 0.1 % in density in the liquid phase below 450 K, 1 % in density at temperatures between (450 and 500) K, 3 % in density at temperatures above 500 K, 1 % in density in the vapor phase and at supercritical conditions below 10 MPa and 450 K, 0.5 % in vapor pressure, and 2 % in heat capacity. Data for the speed of sound are not available to ascertain the uncertainty.

Decane. Experimental measurements for decane and their deviations from the equation of state are summarized in Table 9 and shown in Figures 7 and 8. There are two conflicting groups of data sets for decane in the liquid region. The data of Gouel (1978), Reamer et al. (1942), and Sage et al. (1940) are mutually consistent, and the data of Banipal et al. (1991), Bessieres et al. (2001), Caudwell et al. (2004), Gates et al. (1986), and Susnar et al. (1992) are mutually consistent, but the two sets (Gouel−Sage−Reamer vs Banipal−Bessieres−Caudwell−Gates−Susnar) differ by more than 0.5 % in density. The very recent data of Audonnet and Padua (2004) also compare well with the second set. Aside from the data of Gouel, Reamer et al., and Sage et al., most of the liquid-phase data up to 340 K are represented to within 0.2 % in density. Much of the saturated liquid density data (taken from many different sources) between (290 and 320) K show deviations of less than 0.05 %. Up to 400 K and below 100 MPa, comparisons with the data in the single phase show deviations within the 0.2 % range, with slightly higher deviations at pressures above 100 MPa. Above 400 K, the data of Reamer et al. (1942), which at lower temperatures differed from calculated values by more than 0.5 %, agree reasonably well with the equation. However, the data of Gehrig and Lentz (1983), which compared favorably with the equation below 400 K, start to deviate by more than 1 %.

The data of Zuniga-Moreno et al. (2005) became available after the correlation and analysis were finished for decane. The 148 data points span the liquid phase from (313 to 363) K with pressures up to 25 MPa. The average absolute deviation is 0.013 % with a maximum deviation of 0.04 %. The equation of state compares more favorably with these data than any other data set available in this work, which, considering that the data were not available during fitting, gives high confidence in the correlation for properties in the liquid phase. The measurements of Snyder and Winnick (1970) approach 700 MPa with deviations of 0.5 % at the highest pressures (for example, see the 350 K plot in Figure 7). However, the new data of Zuniga-Moreno et al. may indicate that the data of Snyder and Winnick have higher uncertainties of at least 0.15 % at 350 K and 25 MPa and that the uncertainties most likely increase at higher pressures. Additionally, the Zuniga-Moreno et al. data and other data with similar deviations tend to support the extrapolation of the equation of state to high pressures with smaller uncertainties than those for the data of Snyder and Winnick.

The vapor pressures of decane are quite well-characterized from 270 K to the critical point. Only one source of reliable data (that of Morgan and Kobayashi, 1994) is available at temperatures above 500 K. There are substantial outliers (individual data points that represent either measurement or recording errors) in the available data, but the data sets that appear to be consistent are shown to be within 0.2 % of the equation. The available heat capacity data, which range from (250 to 470) K, are generally fitted to within 1 %, aside from a few data points near the triple point temperature for the saturation heat capacity. The single-phase heat capacity data of Czarnota (1993) were measured at 298 K, and the equation compares well (within 1 %) with these data below 10 MPa but reaches a maximum of 7.5 % at 86 MPa, while deviations are in the 1 % range between (200 and 250) MPa. The equation is within 1 % of the isochoric heat capacity data of Amirkhanov et al. (1991) at temperatures above 660 K, but the deviations increase at lower temperatures approaching the critical point. The equation also agrees well with the liquid-phase speed of sound data up to 500 K to within 1 %, including the measurements up to 50 MPa of Khasanshin and Shchemelev (2001).

The equation of state is valid from the triple point temperature to 675 K with pressures up to 800 MPa, although the uncertainties are substantially higher above 500 K. The uncertainties in density are 0.05 % in the saturated liquid density between (290 and 320) K, 0.2 % in the liquid phase at temperatures to 400 K (with uncertainties up to 0.5 % above 100 MPa), 1 % in the liquid phase up to 500 K, and 2 % at higher temperatures and in the vapor phase. Vapor pressures have an uncertainty of 0.2 %, and the uncertainties in liquid-phase heat capacities and liquid-phase sound speeds are 1 %. The uncertainty in heat capacities may be higher at pressures above 10 MPa.

Hydrogen Sulfide. Experimental measurements for hydrogen sulfide and their deviations from the equation of state are summarized in Table 9 and shown in Figures 9 and 10. The single-phase density data in the liquid for hydrogen sulfide include the measurements of Ihmels and Gmehling (2001) and Reamer et al. (1950). These data were measured near 273 K and higher. The triple point temperature of 187.7 K is nearly 100 degrees below the lower limit of these data. Fortunately, several data sets have been measured down to this low temperature for the saturated liquid state. These low-temperature values include the older data of Klemenc and Bankowski (1932) (with deviations of 0.02 % in density), the more recent data of Cubitt et al. (1987) with deviations less than 0.5 %, and the multiple data points of Clarke and Glew (1970) centered at 194

K with a maximum deviation of 0.04 %. The higher deviations of the data of Cubitt et al. are caused by inconsistencies with the data of Ihmels and Gmehling in the single phase. At temperatures above 270 K, data for the saturated liquid phase show even higher deviations from the older data sets of Bierlein and Kay (1953), Kay and Brice (1953), and Reamer et al. (1950). All of these data are inconsistent with the more recent data of Ihmels and Gmehling.

The equation of state represents the new data of Ihmels and Gmehling below the critical point (and in the liquid phase) with average deviations of 0.05 % in density. The agreement with the data of Reamer et al. (1950) is substantially worse, with deviations of 0.5 %. At higher temperatures, agreement with the Ihmels and Gmehling data at pressures above 20 MPa is similar to that in the liquid phase, but the differences begin to increase at lower pressures, especially near the critical point. Between (400 and 500) K, differences are less than 0.5 %, but at temperatures above 500 K, the deviations are larger, with some points exceeding 2 % in density. The inconsistency among all of the data sets at these high temperatures is more than 5 %, including the data of Straty (1983), Liu et al. (1986), and Rau and Mathia (1982). The equation represents the vapor-phase data of Wright and Maass (1931) generally within 0.2 %. Deviations from the vapor-phase data of Reamer et al. (1950) are substantially higher at 273 K, but decrease at higher temperatures for both the single phase and for the saturated vapor phase.

The equation of state agrees well with most of the vapor pressure measurements. From the triple point to about 360 K, deviations are generally within 0.2 % of the various data available. Near the critical point, the deviations are somewhat larger, but are generally within 0.5 %. There is only one data set containing experimental information for the liquid-phase heat capacity. These data of Giauque and Blue (1936) are generally represented to within 1 %. Three of the data sets for the ideal gas isobaric heat capacity are consistent within 1 %, and the calculations from Marsh et al. (1994) show similar consistency. The values of Barrow and Pitzer (1949) and Felsing and Drake (1936) do not fall within this 1 % range, except at temperatures below 600 K for the data of Barrow and Pitzer. Most of the deviations of the equation from the second virial coefficients are within 5 %. These data range from (250 to 500) K.

The equation of state covers the temperature range from the triple point to 760 K with pressures up to 170 MPa. The uncertainties in density are 0.1 % in the liquid phase below the critical temperature, 0.4 % in the vapor phase, 1 % at supercritical temperatures up to 500 K, and 2.5 % at higher temperatures. Uncertainties are larger near the critical point. The uncertainty in vapor pressure is 0.25 %, and the uncertainty in heat capacities is estimated to be 1 %; however, a lack of available data for the heat capacities and speeds of sound makes it difficult to establish estimated numerical uncertainties for these properties.

2-Methylbutane (Isopentane). Experimental measurements for isopentane and their deviations from the equation of state are summarized in Table 9 and shown in Figures 11 and 12. There are two primary data sets for the liquid, that of Walter et al. (1992) and that of Mopsik (1969). Although the data of Walter et al. are newer by more than 20 years (their stated uncertainty is 0.5 % in density), fitting these data produced systematic errors in other data types, such as the vapor pressure. In the end, the data of Mopsik were used in the determination of the coefficients. There are large discreprencies among the available data in the supercritical region. The apparent systematic deviations in the data of Isaac et al. (1954) are unfortunate, since the data extend up to 573 K, but cannot be used to evaluate the accuracy of the equation. The data of Isaac et al. were not used during fitting, and the final equation relied on the data of Silberberg et al. (1959) at lower pressures and on the data of Vohra and Kobe (1959) at higher pressures. There are no single-phase density data below 200 K, although several saturated liquid densities are available, and the equation agrees with the data to within 0.2 % down to the triple point temperature.

The equation differs from the liquid-phase heat capacities by 1 % at 300 K. The deviations increase with decreasing temperatures, reaching a maximum of 3.5 % at 170 K. The increased deviations at low temperatures possibly result from the long saturation line of isopentane, which may be outside the applicable range of the short form of the fundamental equation. The vapor-phase speeds of sound of Ewing and Goodwin (1991) and the equation agree within 0.03 %, and the liquid-phase speeds of sound of Walter et al. (1992), Houck (1974), and Kling et al. (1953) show general agreement to within 3 %, except for one isotherm at 290 K.

The equation of state is valid from the triple point temperature to 500 K with pressures to 1000 MPa. The uncertainties are approximately 0.2 % in density at temperatures up to 320 K, 0.5 % in density at higher temperatures, 2 % in heat capacity above 250 K, 4 % in heat capacity at lower temperatures, 0.1 % in the vapor-phase speed of sound (over a narrow temperature range from 250 K to 350 K at low pressures), 3 % in the liquid-phase speed of sound, and 0.4 % in vapor pressure at temperatures above 200 K.

2,2-Dimethylpropane (Neopentane). Experimental measurements for neopentane and their deviations from the equation of state are summarized in Table 9 and shown in Figures 13 and 14. There are very few liquid-phase density data for neopentane, and the data points show large scatter. The data of Dawson et al. (1973) appear to be consistent with saturated liquid density data such as those measured by McLure and Barbarin-Castillo (1993). Below 10 MPa, the equation shows deviations of 0.2 % in density. Deviations increase up to 0.4 % at pressures of 30 MPa. The data of Wappmann et al. (1996) show differences with the Dawson data of up to 1 % in density; however, these data extend up to 200 MPa, and the deviations of the equation from these data are within 1 %. In the vapor phase, comparisons of the equation with the data of Heichelheim et al. (1962) and of Dawson et al. are generally within 0.5 % in density. Similar trends are visible in the saturated vapor density data of Dawson et al. At high temperatures (above 470 K), the equation represents the data of Heichelheim et al. and of Beattie et al. (1952b) to within 1 % in density, although the scatter in the data is larger than 1 %. Trends in the immediate vicinity of the critical point are difficult to illustrate because of the large differences in density deviations associated with small changes in pressure, and comparisons illustrating deviations in pressure give a more meaningful assessment. Between (433.14 and 433.84) K, and between (3.16 and 3.21) MPa, the 188 data points of Beattie et al. (1951b) show an average absolute deviation of 0.1 % in pressure, and the 63 data points of Dawson et al. show an average absolute deviation of 0.03 % in pressure.

There are a substantial number of vapor pressure measurements, especially between the triple point and 300 K, to validate the accuracy of the equation. The agreement between the equation and most of these data points is within 0.1 %. This trend is consistent even at higher temperatures (up to the critical point), with a few outliers. The saturated liquid and vapor densities show deviations similar to those in the single phase, except at temperatures above 430 K. All but one of the very limited liquid-phase heat capacities are fitted to within 1.5 %. These data span the temperature range from (258 to 277) K. The vapor-phase heat capacity data of Hossenlopp and Scott (1981) range from (298 to 523) K and show differences of 0.2 %. These data agree well with the vapor-phase speed of sound data of Ewing et al. (1986, 1987) that are represented to within 0.025 %. Heat capacities and speeds of sound are closely related properties, and equations fitted using both data types generally produce lower uncertainties in other properties such as enthalpies and entropies. Nearly all of the liquid-phase speed of sound data shows differences of less than 1 %, with an average of 0.24 %. These data extend up to the critical temperature. There are a substantial number of second virial coefficients from various sources for neopentane. The scatter in the data is up to 20 %, but the majority of the data show differences of 5 % or less from calculated values.

The uncertainties in density in the equation of state range from 0.2 % in the liquid phase at pressures less than 10 MPa to 1 % in the liquid phase at higher pressures (up to 200 MPa) and at temperatures above the critical point (up to 550 K). The uncertainty in density in the vapor phase is 0.5 %. Uncertainties in other properties are 0.1 % for vapor pressure, 2 % for liquid-phase heat capacities, 0.5 % for vapor-phase heat capacities, 1 % for liquid-phase sound speeds, and 0.02 % for vapor-phase sound speeds from (250 to 350) K at low pressures.

2-Methylpentane (Isohexane). Experimental measurements for isohexane and their deviations from the equation of state are summarized in Table 9 and shown in Figures 15 and 16. The liquid-phase data for isohexane are made up of three nonoverlapping data sets. The data of Moriyoshi and Aono (1988) cover the range from (298 to 313) K with pressures to 130 MPa and show deviations of 0.06 % in density. The data of Bridgman (1931) are located at (273, 323, and 368) K with pressures to 1000 MPa and show deviations of 0.12 % in density. The data of Kelso and Felsing (1940) cover the temperature range from (373 to 548) K and have an average deviation of 0.22 %. The data of Griskey and Canjar (1964) overlap the data of Kelso and Felsing but show a systematic offset. There are no data for the vapor phase, aside from a few data points of Kelso and Felsing above the critical temperature. The deviations of these low-density data are generally within 0.6 % in density. In the saturated liquid phase, there are a few data points from (110 to 155) K from Davenport et al. (1966) that compare within 0.5 % with the equation at the lowest temperature and within 0.1 % at the highest temperature. Above 240 K, deviations from the equation are generally within 0.2 % for the data of Awwad and Pethrick (1983) and of Holcomb et al. (1995). At (293 and 298) K, there are about 20 different data sets (most of which contain just one data point) with deviations within 0.05 %.

Between (280 and 350) K, most of the consistent vapor pressure data deviate from the equation by less than 0.2 %. Above 350 K and up to the critical point, the scatter in the data increases with differences of approximately 0.5 %. There are no data below 280 K with uncertainties low enough to validate the equation. The fixed functional form used to fit the properties of isohexane was not able to fit all of the saturated liquid-phase heat capacities, due to the very long saturation line ($T_{\mathrm{trp}}/T_{\mathrm{c}} = 0.24$). Comparisons with the heat capacity data of Douslin and Huffman (1946) show deviations within 2 % except at the lowest temperatures. The data of Czarnota (1998) at 298 K were measured from atmospheric pressure to 760 MPa. Deviations at the lowest pressures are generally within 1 %, with a maximum deviation of 9.2 % at 257 MPa. The deviations of the vapor-phase heat capacity data of Waddington et al. (1949) are generally within 0.1 %. The equation of state represents the speed of sound data for the liquid phase between (233 and 313) K to within 1 %. The speed of sound data of Plantier and Daridon (2005) became available after the correlation and analysis were finished for isohexane. The data span the liquid phase from (293 to 373) K with pressures up to 100 MPa. The average absolute deviation is 0.4 %. These new data expand the range of experimental values significantly. The two data sets available during fitting ranged from (233 to 313) K for the saturation liquid state only (very low pressures). The deviations of the equation of state from the new data are smaller than those of the other two data sets used in fitting. Comparisons with the new data at high pressures are not optimal (approximately 0.5 %), but they demonstrate that the equation of state extrapolates well to high pressures, one of the desired attributes of the Span–Wagner functional form.

The uncertainties in the equation of state are 0.2 % in density in the liquid phase, 0.5 % in density in the vapor phase, 1 % in density above the critical temperature, 0.2 % in vapor pressure between (280 and 350) K, 0.5 % in vapor pressure at higher temperatures, 2 % in heat capacities, and 1 % in the speed of sound.

Krypton. Experimental measurements for krypton and their deviations from the equation of state are summarized in Table 9 and shown in Figures 17 and 18. There is a substantial amount of data for the densities of krypton, although the scatter among the various sets is high. At the lowest temperatures, the data of Barreiros et al. (1982a), Streett and Staveley (1971), and Theeuwes and Bearman (1970a) vary by 0.4 % in density. Some of the differences in the data of Blagoi and Sorokin (1970) are more than 0.75 %. The equation of state shows typical deviations of 0.2 % or less in density for most of the consistent data. Likewise, the available saturated liquid-phase densities show deviations of less than 0.2 %. Beginning with temperatures of around 180 K, the scatter between the data sets increases with the inclusion of the data of Calado et al. (1986). At 190 K, these differences are 0.5 %. At pressures above 100 MPa and at temperatures below 240 K, the equation deviates from the high-pressure data of Streett and Staveley (1971) by up to 1 % or more at the highest pressures. A similar trend exists with the data of Trappeniers et al. (1966) at higher temperatures, and at pressures above 100 MPa. At temperatures above 270 K, most of the data except those from Beattie et al. (1952a) are represented with deviations of less than 0.2 %, with average deviations of 0.1 %. In the vapor phase below the critical temperature, the equation agrees well with the data of Novikov et al. (1974), with maximum deviations of around 0.4 % near the saturation conditions.

Deviations of the equation compared to vapor pressure measurements are within 0.2 %, except at the lowest temperatures where some of the data such as those from Lee et al. (1972) are systematically offset from other measurements. Excluding these data, the equation is in good agreement with values from Bowman et al. (1969), Theeuwes and Bearman (1970b), Michels et al. (1952c), and others. Beaumont et al. (1961) published five isobaric heat capacities that agree within 1 % with the equation. These data are located near the triple point, and there are no other data to compare with at other temperatures. However, there are multiple measurements of the speed of sound over a wide range of temperatures that help validate the thermodynamic surface for both heat capacities and sound speeds. Below 200 K and 20 MPa, the equation shows deviations of less than 1 % for the liquid-phase data. The deviations from the data of Streett et al. (1972) remain within 3 % up to 100 MPa.

There are a large number of second virial coefficients for krypton. Above 260 K, the data are randomly scattered about the equation of state with maximum differences of 5 %. Between (150 and 260) K, the values of the second virial coefficients are uniformly above those calculated from the equation with a maximum difference of about 2.5 %.

The equation of state is valid from the triple point to 750 K with pressures to 200 MPa, although the uncertainties increase substantially above 100 MPa. The uncertainties in density are typically 0.2 % below 100 MPa, increasing to 1 % at pressures up to 200 MPa. The uncertainty in vapor pressure is 0.2 %, and the uncertainties in speed of sound are 0.01 % in the vapor phase (including supercritical conditions) at low pressures, 1 % below 20 MPa in the liquid phase, and 3 % below 100 MPa at other state points. The limited amount of heat capacity data show that the uncertainty is 1 % near the triple point, and uncertainties in heat capacities at other states are probably within 2 %, at least for pressures up to 20 MPa.

Nitrous Oxide. The density of nitrous oxide has been recently measured by Ihmels (2004) as part of the development of the equation of state in this work. These data range from (273 to 523) K in the liquid and supercritical phases with a maximum pressure of 40 MPa. Below the critical temperature, the equation of state represents the data to within 0.1 % in density, aside from a few data points near the saturation pressure and at temperatures approaching the critical point. At temperatures above 320 K, the deviations generally stay within 0.2 %, with several higher deviations at the lower pressures. Above 420 K, the deviations are as large as 0.5 %. The data of Couch et al. (1961) in the liquid phase generally deviate by less than 0.5 % in density from the data of Ihmels. The lowest temperature isotherm of Couch et al. at 240 K is 30 K lower than that of Ihmels, and the equation shows a maximum deviation of 0.2 % for this isotherm. The only information available at lower temperatures is the single saturated liquid density point of Machado et al. (1980) with a deviation of 0.23 % and the saturated liquid densities of Leadbetter et al. (1964) with average deviations of 0.34 %. These data are near the triple point. There are several data sets in the vapor phase; in particular, the calculated values derived from second and third virial coefficients of Hurly (2004) show very good agreement with the equation of state (less than 0.1 % in density), except at his highest pressures where the term for the fourth virial coefficient becomes significant. Other data sets (shown in Figure 19) show similar trends for temperatures up to 303 K and for temperatures above 340 K with pressures less than 10 MPa. Data in the critical region show the highest inconsistencies but generally remain within 1 % in density among the various sources. In particular, the data of Ihmels and of Couch et al. at 340 K disagree by as much as 1 %. This discreprency resulted in higher deviations at 320 K in the equation of state for the data of Couch et al., since the data of Ihmels were used as the primary data.

The scatter in the vapor pressure data (see Figure 20) of nitrous oxide is around 0.3 % at temperatures above 290 K between the data of Couch et al. (1961) and those of Cook (1953). The equation of state was fitted using all of these data, along with the data of Ohgaki et al. (1990) near the critical point. Near the triple point, the equation agrees within 0.05 % to the single data points of Fonseca and Lobo (1989) and of Machado et al. (1980). Comparisons to heat capacity data show that the equation of state is generally accurate to within 3 % in the liquid phase. However, the data of Blue and Giauque (1935) are rather old, and the data of Haase and Tillmann (1994) show high scatter. No other caloric or sound speed data are available in the liquid phase. In the vapor phase, the equation of state shows average deviations of 0.05 % from the sound speed data of Hurly (2003, 2004). Differences between the equation of state and the second virial coefficients are generally within 4 %, excluding the inconsistent data of Johnston and Weimer (1934).

The uncertainties in the equation of state are 0.1 % in density in the liquid and vapor phases between (220 and 300) K, 0.25 % at temperatures above 300 K and at temperatures below 220 K, and 0.5 % in the critical region, except very close to the critical point. The uncertainty in vapor pressure is 0.2 %, that for heat capacities is 3 %, and that for the speed of sound in the vapor phase is 0.05 % above 220 K. The uncertainty of sound speed in the liquid phase cannot be verified by data but is estimated to be within 5 %.

Nonane. Experimental measurements for nonane and their deviations from the equation of state are summarized in Table 9 and shown in Figures 21 and 22. There is only one data set (Scaife and Lyons, 1980) in the liquid phase below 300 K for nonane. Above 300 K and at pressures above 10 MPa, the data from Scaife and Lyons are inconsistent with the data of Grindley and Lind (1978) and Doolittle (1964) but are consistent with the data of Boelhouwer (1960). New experimental data at the same experimental conditions are required to resolve this inconsistency. The offset of the data of Scaife and Lyons at 300 K remains somewhat constant in comparisons of calculated values from the equation of state down to the lowest temperatures (240 K) of the data. At pressures below 10 MPa, the equation represents the data of Banipal et al. (1991) on average to within 0.07 % in density. Above 300 MPa, the equation shows a maximum deviation of 0.6 % at 800 MPa from the data of Grindley and Lind. The data of Doolittle at 500 MPa and 370 K do not demonstrate the systematic behavior of the data of Grindley and Lind. At higher temperatures, the Grindley and Lind data were used to fit the equation (at pressures below 300 MPa), and a small offset between these data and those of Doolittle at 420 K is evident in the comparisons to the equation of state. Above 500 K, the differences between the equation and the data increase in some situations to more than 1 % in density.

The agreement between the available saturated liquid density data is quite good. The equation fits nearly all of the data within 0.15 % between (240 and 400) K. Furthermore, the uncertainty in the equation between (280 and 335) K is most likely less than 0.05 % in the saturated liquid density, based on the numerous available measurements. The only available experimental data in the vapor phase are the saturated vapor density data of Amirkhanov et al. (1991). These data are fit to within about 1.3 % with both positive and negative deviations, with a few outliers caused by the scatter in the data. There are very few vapor pressure measurements outside the temperature range from (310 to 430) K, none of which are accurate enough to validate the equation. There are, however, a large number of measurements at the normal boiling point, many of which vary by more than 3 %, with the majority of the data located within 0.2 % of the equation. Data at lower temperatures (down to 310 K) are also fitted to within 0.2 %. The accuracy of the equation outside this range cannot be verified by data but is estimated to be within 0.5 % above 430 K. Comparisons against the generalized vapor pressure equation of Lemmon and Goodwin (2000) show a maximum deviation of 0.3 % above 430 K and a deviation of 0.8 % at 225 K. The generalized equation used one functional form to fit the vapor pressure measurements from methane to hexatriacontane.

The experimental data for nonane include both isobaric and isochoric heat capacity information. Below 550 K, the equation compares reasonably with these data (with all points located within 2 %). Above 550 K, the deviations from the critical region data increase up to a maximum of 3 % at the highest temperatures. The deviations are even higher near the critical point. There are a limited number of saturation heat capacities as well at temperatures below 320 K, with 2 % deviations down to 233 K. At lower temperatures near the triple point, a maximum deviation of +3.5 % occurs for one data set and +2.5 % for another. Most of the data for the liquid-phase speed of sound show deviations of less than 0.5 %. Nonane is very well characterized by experimental data for the speed of sound below 430 K in the liquid, but additional measurements are needed at higher temperatures and in the vapor phase.

The equation of state is valid from the triple point to 575 K with pressures to 800 MPa. The uncertainties in the equation are 0.1 % in the saturated liquid density between (280 and 335) K and 0.2 % in density in the liquid phase below 430 K and 10 MPa. The uncertainty increases to 0.3 % up to 100 MPa and 0.5 % up to 800 MPa. In the vapor phase and for supercritical states, the uncertainty in density is 1 %, whereas in the liquid phase between 430 K and the critical point it is 0.5 % in density. Other uncertainties are 0.2 % in vapor pressure between (300 and 430) K, 0.5 % in vapor pressure at higher temperatures, 2 % in heat capacities below 550 K, 5 % at higher temperatures, and 1 % in the liquid-phase speed of sound below 430 K.

Sulfur Dioxide. Densities of sulfur dioxide have been measured from (323 to 523) K at pressures up to 32 MPa by Kang et al. (1961) and Hellwig (1955) and in the doctoral dissertations of Hirth (1958) and Kang (1960). These data extend down to temperatures of 270 K in the vapor phase. The recent measurements of Ihmels et al. (2003) extend the measurements of compressed liquid densities down to 273 K at pressures to 35 MPa. The residual part of the Helmholtz equation of state reported here was also reported in the publication of Ihmels et al. Below 273 K, the only available density data are five saturated liquid density points of Seyer and Peck (1930) down to 223 K. These five data points (which were not used in developing the equation of state reported here) are represented by the equation to within 0.05 % in density, although the deviations are higher (reaching up to 0.6 %) for their data at temperatures above 273 K.

Deviations between the experimental density data and the equation of state are shown in Figure 23. The densities measured by Ihmels et al. are represented with an average absolute deviation of 0.06 %. The density data of Kang (1960), Kang et al. (1961), and Hirth (1958) are represented with average absolute deviations of 0.29 %, 0.37 %, and 0.11 %, respectively, excluding their values in the critical region. Below 390 K, there are small differences among the available data (e.g., the differences between the data of Ihmels et al. and Kang et al. are approximately 0.2 %). The vapor-phase data of Hirth (the only data available in the vapor below 370 K) are represented generally within 0.1 % as shown in Figure 23. As the critical region is approached, the deviations in the data tend to spread with differences exceeding 1 % near the critical point. These large differences occur in the critical region where experimental techniques are the most difficult for the measurement of density. At temperatures above the critical point, the differences between the data of Ihmels et al., Kang, and Hellwig increase to above 1 %.

The equation represents the calculated ideal gas isobaric heat capacities of Gordon (1961), Evans and Wagman (1952), and McBride and Gordon (1961) to within 0.15 % (the upper temperature limit is 6000 K). The calculated data of Barrow and Pitzer (1949), Cross (1935b), Kobe and Long (1950), and Nagarajan (1963) deviate systematically above 400 K from these data. Comparisons of the saturated liquid isobaric heat capacity data of Giauque and Stephenson (1938) and Riedel (1939) are within 0.6 %. There are considerable differences between the various data sets for vapor pressure as shown in Figure 24. At temperatures below 270 K, the data of Giauque and Stephenson and of Stock (1923) differ by about 0.4 % or more. At temperatures above 360 K, the data of Kang (1960) agree with other data, but the data at temperatures from (323 to 360) K differ by up to 2.2 %. In the middle range (280 K to 330 K), the data of Brady and O'Donnell (1968) and of Hirth (1958) agree within about 0.2 %.

The equation of state for sulfur dioxide is valid from the triple point to 523 K with pressures up to 35 MPa. The uncertainty in density of the equation of state ranges from 0.1 % at low temperatures in the liquid and vapor phases to 0.5 % at the highest temperatures. The uncertainty in heat capacities is 2 %, and the uncertainty in vapor pressure is 0.4 % at temperatures above 270 K. The uncertainty in vapor pressure increases at lower temperatures due to the lack of reliable experimental data. In the critical region, the uncertainties are higher for all properties except vapor pressure.

Toluene. The amount of experimental data available for toluene is more than that of any other fluid studied in this work. Additionally, measurements of toluene have been part of a round robin to ascertain experimental uncertainty among some of the best laboratories in the world (Bean, 1999; Magee and Bruno, 1996; Masui, 2002; Watson, 2000; Weber, 2004). Other measurements have been made during the same time at other institutes (Ihmels and Gmehling, 2001; Avelino et al., 2003; etc.) The differences among these data represent the smallest uncertainties for the fluids studied here, as shown in Figures 25 to 30. For example, the uncertainty in the equation of state for the saturated liquid density approaches 0.01 % around 300 K due to the excellent agreement among many different sources. A standard reference equation (very high accuracy) will be developed after final measurements have been made and will replace the equation presented here. This new equation will be used in developing new transport property equations for toluene.

Because of the large amount of data available, the deviations of the equation of state from the data have been expanded into multiple figures. Figure 25 shows comparisons of the equation of state to single phase $p\rho T$ data. The data of Magee and Bruno (1996) are the only data between (180 and 220) K. These data are of high accuracy and show deviations of less than 0.05 % in density. At 220 K, the data of Avelino et al. (2003) show differences of less than 0.05 % from the data of Magee and Bruno. These differences are slightly higher with increasing temperatures (up to 0.08 % at 400 K). The data of Ihmels and Gmehling (2001) begin at 273 K and show comparable deviations to those of the data of Magee and Bruno at this temperature. The equation of state is within 0.05 % of both data sets. At (290 to 300) K, several other data sets appear with differences generally within 0.1 %. Up to 50 MPa, the equation deviates from these data by no more than 0.075 %, and at 175 MPa, the deviations are generally all within 0.15 %. A systematic deviation from the data is evident in the equation above 100 MPa and approaches 1 % at pressures up to 1 GPa. The trends in the data and the equation of state at 290 K are quite similar to those at higher temperatures up to the critical region. The comparisons with saturated liquid densities (see Figure 27) show similar trends, with most of the data fitted within 0.05 %. Between (285 and 330) K, there is a substantial grouping of data with deviations less than 0.05 % as compared to values calculated from the equation of state. Of the 130 data points available at 298 K, 100 points fall within 0.04 %, 80 within 0.02 %, and 50 within 0.01 %. The data with the lowest experimental uncertainties (Bean, 1999) show deviations of 0.002 % (even though they were not used in the fit).

Above 540 K, the deviations in the critical region start to increase, and some are higher than 1 % near the critical point. Above this temperature, the scatter among the data sets increases dramatically, and the equation of state agrees well with some of the data of Straty et al. (1988) and, at pressures above 20 MPa, with some of the data of Akhundov and Abdullaev (1971). Near the critical pressure, these two data sets disagree by more than 1 % (with the equation biased toward the data of Straty et al.) Neither data set was used in the fitting of the equation of state. There are only a limited number of data sets for the vapor phase. The data of Opel et al. (1974) were measured at the lowest temperatures (starting at 393 K). The comparisons with the equation of state show an average deviation of 0.05 %. The data of Marcos et al. (1983) show somewhat similar deviations but with higher scatter. The saturated vapor-phase data of Akhundov and Abdullaev (1977) show deviations of less than 0.25 % up to 545 K. The deviation plot for the saturated vapor density (Figure 30) shows a discontinuity in the data at 420 K (their data below 420 K show negative deviations of −0.2 % at most, and their data above 420 K show positive deviations of about 0.08 %).

The vapor pressures from (305 to 425) K are very well characterized, with approximate deviations of 0.05 % as shown in Figure 26. Below 305 K, there are data down to 270 K with deviations of about 0.3 %. It is not clear which of these data are the most accurate, and additional measurements are needed from 305 K down to the triple point to validate the accuracy of the equation given here. Above 425 K, the equation represents much of the data within 0.1 % up to 555 K, but there appear to be some systematic deviations in individual data sets. Near the critical point, the deviations increase to 0.15 %.

Figure 28 illustrates the vast number of measurements for the isobaric heat capacities for toluene. Deviations are within 0.5 % or better below 560 K. The deviations are larger near the critical temperature. Span and Wagner (2003a−c) give details on the behavior of the functional form used here near the critical point. The equation deviates from the speed of sound data shown in Figure 29 by less than 1 % up to 100 MPa, and within 2 % at higher pressures. Deviations in the critical region are higher. There are no high accuracy measurements for the speed of sound in the vapor phase. Figure 30 shows that the data for the enthalpy of vaporization are generally fit within 1 % and that deviations with the saturation heat capacities are small (similar to those for the isobaric heat capacities). The ideal gas heat capacities, also shown in this figure, deviate by up to 1 % from the limited data available. The calculated values of Marsh et al. (1994) were used to fit the coefficients for the ideal gas equation used in this work, with very close agreement above 200 K.

The equation of state is valid from the triple point to 700 K with pressures to 500 MPa. The uncertainties in density in the equation of state are 0.05 % in the liquid phase up to 540 K, 0.5 % up to the critical temperature, 1 % at higher temperatures, 0.5 % at pressures from (100 to 500) MPa, and 0.2 % in the vapor phase. The uncertainty for the saturated liquid density is as low as 0.01 % at temperatures near 300 K. The uncertainties in vapor pressure are 0.3 % from (270 to 305) K, 0.05 % from (305 to 425) K, 0.1 % up to 555 K, and 0.15 % up to the critical temperature. The uncertainty in heat capacities is generally 0.5 % and rises to 3 % in the critical region. The uncertainty in the speed of sound is 1 % up to 500 K and 100 MPa and rises to 2 % at higher pressures and higher temperatures.

Xenon. The liquid-phase data of Streett et al. (1973), Theeuwes and Bearman (1970c), and Ulybin et al. (1974) are relatively consistent at low temperatures for xenon. Near the triple point, the equation of state and all three data sets agree within 0.05 % in density. At increasing temperatures, the agreement decreases. At 220 K, the equation shows differences of 0.2 %, and at 240 K, the equation differs from the data of Ulybin et al. by less than 0.1 % and by 0.4 % from the data of Straty et al. At 260 K, the data of Baidakov et al. (1992) differ from the data of Streett et al. by 0.7 %. The data of Baidakov et al. were selected in fitting over the data of Streett et al. because of their agreement with other data. The disagreement of the Streett et al. data is also shown in the (280 and 290) K plots in Figure 31 between (10 and 100) MPa. The differences between the data sets of Streett et al. and Michels et al. (1954) are generally about 0.5 %, whereas the data of Ulybin et al. and of Michels et al. agree very well.

The vapor phase of xenon is characterized by the data of Hurly et al. (1997) (with deviations of 0.03 %), Michels et al. (1954), and Ulybin et al. (1974) as shown in Figure 31. These data sets are relatively consistent, except near the critical point. At temperatures above the critical temperature, the calculated values of density deviate systematically from the data of Michels et al. Additional measurements are needed to verify the true behavior of xenon at supercritical temperatures. However, for the most part the deviations remain within 1 % in density.

The equation of state deviates from vapor pressure measurements by up to 0.2 % as shown in Figure 32. The scatter in the data is highest below 200 K and lowest above 250 K, where deviations are within 0.1 %. Deviations are generally 0.2 % near the triple point, excluding some of the older data sets. Measurements of the speed of sound deviate by as much as 0.5 % in the liquid phase and 0.05 % in the vapor phase (compared to the data of Hurly et al., 1997). The deviations from the data of Pitaevskaya et al. (1975) at their lowest pressures (40 MPa) are greater than 1 %, but the accuracy of these data cannot be confirmed. At (60, 80, and 100) MPa, their deviations are smaller (on the order of 1 %) but increase as the pressure rises to 400 MPa. The equation of state is not able to accurately represent the speed of sound data in the critical region (except for the points furthest removed from the critical point) of Kline and Carome (1973) or Gillis et al. (2004). The limited number of data points from Clusius and Riccoboni (1938) for the isobaric heat capacity near the triple point temperature are represented to within 1 % by the equation of state. There are a substantial number of second virial coefficients for xenon, and Figure 32 shows that the scatter in the data is about 7 %, with the majority fitted to within 3 %. The uncertainties in the equation of state are 0.2 % in density up to 100 MPa, rising to 1 % at higher pressures, 0.2 % in vapor pressure, 1 % in the speed of sound, and 2 % in heat capacities.

Hexafluoroethane—R-116. Experimental measurements for R-116 and their deviations from the equation of state are summarized in Table 9 and shown in Figures 33 and 34. Of all the fluids studied in this work, R-116 appears to be the fluid with the least reliable data. Oddly enough, it is also the fluid with the largest number of different data types. The density behavior of the equation in the single-phase regions is based upon two data sets: the liquid-phase data of Maslennikov (1994) and the vapor-phase data of Kijima et al. (1977). In the region where these two data sets overlap (above the critical temperature), the agreement is quite poor, with differences often greater than 1 % in density. For the saturated liquid density, the data of Gunchuk et al. (1989) show comparisons with the equation within 0.2 %.

The available data for the vapor pressure show that calculations from the equation of state are within 0.3 % between 175 K and the critical temperature. In particular, the recent data of Kao and Miller (2000) differ by no more than 0.14 % from values calculated using the equation between (200 and 285) K. These data are also in very good agreement with the data of Kleiber (1994). The available data for the speed of sound are all located in the vapor phase. The equation differs from the data sets of Hurly (1999) and Hurly et al. (2003) on average by less than 0.1 %. The data of Jarvis et al. (1996) show higher deviations in regions overlapping the data of Hurly.

There are three data sets in the liquid and supercritical phases of R-116 for the isobaric heat capacity. These data include the low-temperature data of Pace and Aston (1948) (with deviations less than 0.5 %), the wide ranging data of Kim (1974), and the critical region data of Hejmadi et al. (1977). Deviations from the data of Hejmadi et al. range from (1 to 25) %. However, this is not surprising due to the sharp rise in the values of the heat capacity (from 770 to 4443 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) at these near critical state points. The data of Kim (1974) show an offset from the equation of about 6 %. The data cover both the liquid and vapor phases and seem to be in disagreement with the calculated ideal gas isobaric heat capacity information from Chen et al. (1975b). The data of Kim (1974) were not used in the final fit. Both Hejmadi et al. and Kim derived their heat capacities from enthalpy data (which were also reported in their papers), and Kim additionally reported isothermal throttling coefficients. The uncertainties in the equation are 0.5 % in density for liquid and vapor states and 1 % in density or pressure for supercritical states. For vapor pressures, the uncertainty is 0.3 %, that for vapor-phase sound speeds is 0.2 % and that for heat capacities is 5 %.

1,1-Dichloro-1-fluoroethane—R-141b. Comparisons with the experimental data for R-141b are shown in Figure 35 for single-phase densities and in Figure 36 for saturation properties, speeds of sound, and ideal gas isobaric heat capacities. Density data in the liquid are available at temperatures down to near the triple point temperature. However, due to decomposition of the fluid, there are no experimental density data (aside from the critical point) above 400 K. The data of Defibaugh et al. (1993) were updated in their 1997 publication (Defibaugh and Moldover), and the older data are not considered here. The equation of state represents the data of Duarte-Garza et al. (1997), Defibaugh and Moldover (1997), and Matsuo et al. (1994) all within 0.1 % in density. The high-pressure data of Malhortra and Woolf (1994) disagree with other data in similar regions by as much as 0.6 %. However, the data show that the equation is valid up to pressures of 400 MPa, at least within 0.5 % in density. The vapor-phase data of Weber (1991) and the equation of state differ by less than 0.05 %. Higher differences (up to 0.5 %) are seen with the vapor-phase data of Duarte-Garza et al. near saturation conditions.

There is remarkable consistency between the measured vapor pressures from 270 to 400 K. Most of the available data are represented within 0.15 %. Below 270 K and above 400 K, the inconsistencies increase but are still within 0.6 %. There are no reliable vapor pressure measurements below 250 K. Likewise, nearly all of the saturated liquid densities except those measured by Maezawa et al. (1991b) are consistent and agree with values from the equation of state to within 0.1 % in density.

There are two data sets for the speed of sound. The data of Goodwin and Moldover (1991), with an AAD of 0.007 %, were measured for the vapor phase, and the data of Takagi and Hongo (1993), with an AAD of 0.2 %, were measured for the liquid phase. Unfortunately, there are no isochoric or isobaric heat capacities for the liquid phase, and the uncertainties of these properties calculated from the equation of state are unknown. For the ideal gas, there are few data points for the isobaric heat capacity, with the equation relying on the calculations of Goodwin and Moldover derived from their speed of sound measurements. Calculated values from Marsh et al. (1994) were used to supplement these measurements at higher and lower temperatures.

The equation of state for R-141b is valid from the triple point to the onset of decomposition of the fluid and at pressures to 400 MPa. The equation has uncertainties of 0.2 % in density between (180 and 400) K and at pressures to 100 MPa, and 0.5 % in density at higher pressures. The uncertainty in density may be higher as temperatures approach 400 K. Vapor pressures are represented with an uncertainty of 0.2 % from (270 to 400) K. The uncertainty in speed of sound is 0.01 % in the vapor phase between (250 and 350) K and at low pressures and 0.5 % in the liquid phase. Heat capacity data are not available to verify the equation of state; however, the uncertainties are estimated to be within 5 %.

1-Chloro-1,1-difluoroethane—R-142b. The data situation for R-142b is not very good, even though experimental information is available for states above the critical temperature. In the liquid phase as shown in Figure 37, the data of Sousa et al. (1992a) are represented to within 0.03 % in density between (293 and 370) K. Deviations of nearly 1 % are seen in their last isotherm at 403 K at a pressure near the critical pressure, but the deviations are lower as the pressure increases along this isotherm. Other data in the liquid phase differ by (0.2 to 0.4) % from the data of Sousa et al., including the data of Strom and Gren (1993) and Maezawa et al. (1991a). The differences with the Maezawa et al. data are also seen in comparisons with their saturated liquid densities (as shown in Figure 38). The equation of state is validated in the vapor phase by the data of Riedel (1941) and of Dressner and Bier (1993), and comparisons with the equation are generally within 0.2 % (below 375 K). There are additional measurements of the saturated vapor densities, but the scatter in these data sets is large, and the equation is based solely on the single-phase points. The one exception to this is the data of Tanikawa et al. (1992). These data are located near the critical point and the equation shows deviations of less than 1 % for most of the points (similar to deviations in their measurements for the saturated liquid in the critical region). The critical point used in this work for R-142b was taken from Tanikawa et al. Near the critical point, the data sets of Fukushima and Watanabe (1992) and Yada et al. (1991) show some scatter, and these data sets agree neither with each other nor with the high-temperature isotherm of Dressner and Bier. Their measured densities differ by as much as 1 %, with increasing differences closer to the critical point.

There is also significant scatter in the measured vapor pressures as shown in Figure 38. Much of the data are within 0.5 % of the equation of state. The values of Silva and Weber

(1993) (with temperatures up to 290 K) were used in fitting, and the data of Fukushima and Watanabe (1992) and Yada et al. (1991) were used at higher temperatures. Most of the data from these three sets are represented to within 0.2 %. There are several sets of data for the liquid isobaric heat capacity, with deviations less than 1.5 % for the data of Nakagawa et al. (1993). The data of Perlick (1937b) differ by as much as 3 % from other data sets but are the only heat capacity data with values down to 150 K. There are also a limited number of data sets for the ideal gas isobaric heat capacity. The scatter between the data sets is as high as 1.5 %.

The vapor-phase speed of sound data of Beckermann and Kohler (1993) differ from the equation by 0.03 %. Komarov et al. (1967) published saturated vapor-phase speed of sound data, but these data differ by up to 6 % at the lowest temperatures (263 K). Between (310 and 383) K, the data differ by less than 1 %. Comparisons with their data in the liquid show deviations less than 1 % between (283 and 363) K. The deviations are substantially higher outside of this region. The second virial coefficient data of Beckermann and Kohler (1995) are represented to within about 1.5 %. Other sources show deviations of up to about 5 %.

The equation of state is valid from the triple point temperature to 470 K with pressures to 60 MPa. Although experimental density data are only available down to 190 K, the extrapolation behavior was checked between this temperature and the triple point temperature. In addition, the fixed functional form used to fit the equation helps to ensure that the equation exhibits proper behavior, even in the absence of data. The uncertainties in density are 0.3 % in the liquid phase below 370 K, 1 % at higher temperatures in the liquid and supercritical regions and 0.5 % in the vapor phase. Uncertainties for other properties are 0.5 % for vapor pressure, 2 % for heat capacity and liquid-phase sound speed, and 0.2 % for vapor-phase sound speed.

Octafluoropropane—R-218. Experimental measurements for R-218 and their deviations from the equation of state are summarized in Table 9 and shown in Figures 39 and 40. There are two sets of density measurements in the liquid phase for R-218. In their overlapping range from (240 to 340) K, these two sets agree within 0.25 % in density, with the equation deviating by 0.2 % (on average) from the data of Defibaugh and Moldover (1997), and by 0.16 % from the data of Bouchot and Richon (1997). Both data sets appear to disagree with the saturated liquid density data of Brown (1963) at temperatures between (220 and 280) K, and the values at saturated liquid states from the equation of state are determined solely by the single-phase data used in the fit. At temperatures above the critical temperature, the deviations from the data of Defibaugh and Moldover (which extend to 370 K) are generally within 1 % in density, with the highest deviations at pressures less than 4 MPa. At higher pressures, the deviations are within 0.2 %. The data of Defibaugh and Moldover at temperatures above 340 K show pressure deviations that are generally within 0.5 %. The data situation in the vapor phase is of some concern. The equation represents the data of Bouchot and Richon well at (313 and 333) K at pressures less than 1 MPa but does not represent other vapor-phase data at lower temperatures. Additional measurements in this region would help clarify the vapor-phase behavior of R-218. At the highest temperatures (between 370 K and 440 K), the older data of Brown (1963) show deviations in pressure of around 0.8 %. Deviations in the data of Defibaugh and Moldover are about 0.3 % in pressure at their highest temperature.

The available data for the vapor pressure of R-218 show significant scatter. Between (260 and 343) K, the data of Bouchot and Richon (1997) and Vladimirov and Shvets (1989) agree within 0.4 %, and the equation represents these data to within 0.2 % and 0.14 %, respectively. The agreement with other data sets is not as good. There is very little information on the ideal gas heat capacities for R-218. The equation was fitted in part to the data of Masi et al. (1954) and to calculations from Marsh et al. (1994). Pace and Plaush (1967) measured the saturation heat capacity between (125 and 230) K, and deviations between the equation and these data are generally within 1 %. Beljeva et al. (1997) measured the liquid speed of sound and Vacek et al. (2001) measured the vapor speed of sound. The equation shows an AAD for both of these data sets of about 0.5 %.

The only experimental data for R-218 below 220 K are several vapor pressures and the saturated heat capacity data. The extrapolation behavior of densities below 220 K was checked carefully, and the equation appears to extrapolate well to the triple point temperature. This is verified by the saturation heat capacity data that extend to 125 K.

The upper limit of the equation is 440 K with pressures to 20 MPa. The uncertainty in density is 0.2 % for the liquid phase and 0.5 % for the vapor phase. Above the critical temperature, the uncertainties are estimated to be 1 % in density and 0.5 % in pressure. Calculated vapor pressures have an uncertainty of 0.5 % and that for heat capacities and sound speeds is 1 %.

1,1,1,3,3-Pentafluoropropane—R-245fa. Experimental measurements for R-245fa and their deviations from the equation of state are summarized in Table 9 and shown in Figures 41 and 42. The equation of state represents all of the density data of Defibaugh and Moldover (1997), which span the temperature range from (252 to 372) K, to within 0.1 %, and nearly all of the density data of Bobbo et al. (2003) to within 0.1 %, excluding their 343 K isotherm (the highest that they measured). The data of Grebenkov et al. (2004) are all represented up to 400 K to within 0.2 %. The pressures for these three data sets in the liquid phase are all less than 25 MPa. The liquid-phase densities of Sotani and Kubota (1999) extend up to 200 MPa. At their lowest pressures for the four measured isotherms, the data differ from those of Defibaugh and Moldover by about 0.15 %. The equation of state represents all of the density data of Sotani and Kubota, even up to 200 MPa, for the (313 and 323) K isotherms to within 0.15 %. For the 298 K isotherm, the deviations exceed 0.2 % above 80 MPa, with a maximum deviation of 0.5 % at 200 MPa. For the 303 K isotherm, the deviations exceed 0.2 % above 130 MPa, with a maximum deviation of 0.3 % at 200 MPa.

In the vapor phase, calculations from the equation of state pass through the average of the data of Sotani and Kubota (1999) and Di Nicola (2001). At their lowest temperatures of around 313 K, the data of Sotani and Kubota are about 1 % greater than the calculations from the equation of state and the data of Di Nicola are about 1 % less than the calculations. At the highest temperatures where the data coexist, the data of Sotani and Kubota are about 0.4 % higher and the data of Di Nicola are about 0.5 % lower than the equation. The only experimental data above 372 K are the measurements of Grebenkov et al. (2004). In the vapor phase and in overlapping regions with the data of Sotani and Kubota (298 K to 343 K), the data are systematically higher (AAD of 1 %) than the Sotani and Kubota values (AAD of 0.27 %), with the bias nearly equal to the AAD for each author. At higher temperatures (up to 420 K), deviations from the data of Grebenkov et al. range from about 0.5 % at the lowest pressures to 2 % at their highest pressures in the vapor phase. Above 430 K, the deviations tend to all be within 3 % in density. Saturated liquid densities compare favorably, with most of the deviations within 0.2 % below 400 K. The saturated liquid densities above 400 K and all of the saturated vapor densities of Grebenkov et al. are typically within 2 % of calculations from the equation, even near the critical point.

For the representation of vapor pressures, the equation of state shows deviations of 0.2 % or less for the majority of the data, particularly for the data of Bobbo et al. (2001), Di Nicola (2001), Grebenkov et al. (2004), and Pan et al. (2006). The data of Wang and Duan (2004) are also within this error range at temperatures above 280 K. Toward the upper temperature limit, the data of Pan et al. and of Wang and Duan are quite consistent, but differ from the data of Grebenkov et al. by up to 0.4 %. Additional measurements in this region would help clarify this discreprency.

There is one data set for the isobaric heat capacity in the liquid phase. The equation differs from these data systematically by 5 %. The equation differs from the ideal gas isobaric heat capacity data of Scott (2004) by about 0.2 %. The deviations of calculated liquid-phase speeds of sound are within 0.25 % of the data of Grebenkov et al.

From these comparisons and an assessment of the uncertainties of the experimental data, the estimated uncertainty in the equation of state for density is 0.1 % in the liquid phase below 400 K with pressures up to 30 MPa. Above 30 MPa, the uncertainties are 0.2 % at temperatures above 310 K and up to 1 % for lower temperatures. In the vapor phase and at temperatures above 400 K, the uncertainty is 1 % in density, with higher uncertainties in the critical region. The uncertainty in vapor pressure is 0.2 % above 250 K, and rises to 0.35 % above 370 K. The uncertainties in other properties are 5 % in liquid-phase heat capacities and 0.2 % in liquid-phase sound speeds below 360 K, with unknown uncertainties outside of these regions due to a lack of experimental data.

Fluoromethane—R-41. Experimental measurements for R-41 and their deviations from the equation of state are summarized in Table 9 and shown in Figures 43 and 44. The data situation for R-41 is one of the best (aside from toluene) of the fluids studied in this work. Not only are there highly accurate densities over most of the liquid and supercritical states, there are also accurate isochoric heat capacity data. The fixed 12-term functional form was capable of fitting the data generally within the uncertainties given in Table 1, but the uncertainties in the equation of state were still greater than those for the high accuracy data of Magee et al. (1998). The coefficients given in Table 8 are those fitted using the fixed functional form, consistent with those reported for the other fluids in this work. To improve the accuracy of properties calculated using the equation of state, the temperature exponents in the functional form were adjusted (in addition to the coefficients of each term), similar to that done for dodecane (Lemmon and Huber, 2004) and the butenes (Lemmon and Ihmels, 2005). Comparisons between the two fits (one with the fixed form and one with adjusted temperature exponents) showed very similar results in most of the properties except density and heat capacity. Vapor pressures, virial coefficients, and sound speeds were nearly identical and isochoric heat capacities changed from an offset of up to 2 % at the lowest temperatures for the fixed functional form to deviations of nearly zero for the modified equation. Below 285 K, the fixed functional form was off by +0.3 % in density at the lowest temperature and −0.18 % around 250 K for the data of Magee et al. In this same region, the average absolute deviation for the modified equation compared against these same data was 0.01 % with a maximum offset of 0.06 %. Above 350 K, the deviations from the fixed form are all within 0.23 % while the deviations for the modified form are all within 0.12 %. This application of the fixed functional form with modified temperature exponents demonstrates how higher accuracies can be obtained for fluids with superior data while still maintaining a short equation with proper extrapolation behavior. Figure 43 shows additional comparisons of density measurements with the equation using the modified form. Although there are limited data in the vapor phase (starting at 273 K), comparisons are generally within 0.1 % outside of the critical region. Even in the supercritical region, except at densities near that of the critical density, comparisons show that the equation of state characterizes the data with similar uncertainties. Very near the critical point, the deviations in density increase substantially among the various data sets, but deviations in pressure are mostly within 0.5 %.

The scatter among the various data sets for the vapor pressure is up to 1 %. The modified equation was fitted to the data of Magee et al. (1998) (AAD of 0.09 %). The data of Oi et al. (1983) extend down to the triple point and deviate from the equation by up to 0.25 % at temperatures above 145 K and by up to 0.7 % at lower temperatures. The scatter is higher in the critical region, with differences between the data of Magee et al. and the data of Biswas et al. (1989), Demiriz et al. (1993), and Bominaar et al. (1987) as high as 0.7 %. The modified equation deviates from the isochoric and saturation heat capacity data of Magee et al. by about 1 % or less, except near the critical region for the saturation data and at the lowest densities for the isochoric heat capacity data. There are a significant number of high quality second virial coefficients available for R-41. The equation compares quite favorably with all of these data, with differences generally within 2 %. The maximum deviation of the vapor-phase speed of sound data of Scott et al. (1998) is 0.2 %.

The comparisons shown in Figures 43 and 44 were calculated from the modified equation with varying temperature exponents. This equation is recommended for calculating thermodynamic properties rather than that for the fixed functional form. The ideal gas Helmholtz energy part of the equation is identical to that used in the fixed functional form (with the coefficients given in Tables 5 and 6), but the residual part of the Helmholtz energy that results in the lower uncertainties is represented with the following equation:

$$\alpha^{\mathrm{r}}(\delta,\tau) = n_1\delta\tau^{0.52} + n_2\delta\tau^{1.12} + n_3\delta\tau^{4} + n_4\delta^3\tau^{0.03} + n_5\delta^7\tau^{0.63} + n_6\delta\tau^{3.4}\exp^{-\delta} + n_7\delta^2\tau^{2.2}\exp^{-\delta} + n_8\delta^5\tau^{1.5}\exp^{-\delta} + n_9\delta\tau^{0.1}\exp^{-\delta^2} + n_{10}\delta\tau^{4.8}\exp^{-\delta^2} + n_{11}\delta^4\tau^{3.5}\exp^{-\delta^2} + n_{12}\delta^2\tau^{15}\exp^{-\delta^3} \quad (28)$$

where $n_1 = 1.6264$, $n_2 = -2.8337$, $n_3 = 0.0010932$, $n_4 = 0.037136$, $n_5 = 0.00018724$, $n_6 = -0.22189$, $n_7 = 0.55021$, $n_8 = 0.046100$, $n_9 = -0.056405$, $n_{10} = -0.17005$, $n_{11} = -0.032409$, and $n_{12} = -0.012276$.

The equation of state is valid from the triple point temperature to 425 K with pressures to 70 MPa. The uncertainties in the equation are 0.1 % in density (except near the critical point), 0.25 % in vapor pressure, 1 % in heat capacities, 0.2 % in the vapor-phase speed of sound, and 3 % in the liquid-phase speed of sound. The liquid-phase speed of sound uncertainty is an upper estimate and cannot be verified without experimental information. The uncertainties above 290 K in vapor pressure may be as high as 0.5 %.

Table 10. Calculated Values of Properties from the Equation of State to Verify Computer Code

fluid	temp (T/K)	density (ρ/mol·dm^{-3})	pressure (p/kPa)	enthalpy (h/J·mol^{-1})	entropy (s/J·mol^{-1}·K^{-1})	isochoric heat capacity (c_v/J·mol^{-1}·K^{-1})	isobaric heat capacity (c_p/J·mol^{-1}·K^{-1})	speed of sound (w/m·s^{-1})
acetone	510	4	4807.955	51782.004	157.331	138.449	3766.619	125.351
carbon monoxide	134	10	3668.867	4838.507	41.601	38.702	1642.142	168.632
carbonyl sulfide	380	7	6498.429	16511.877	51.563	55.861	4139.578	161.717
decane	619	1	2071.024	89742.551	164.787	437.033	1043.328	74.576
hydrogen sulfide	375	10	9289.914	15571.227	49.880	42.574	2645.392	248.512
isopentane	462	3	3458.617	37318.534	94.634	190.631	4660.943	96.324
neopentane	435	3	3256.677	34334.720	92.525	184.435	5161.767	93.352
isohexane	499	2	3058.918	48733.743	113.316	233.627	1129.814	90.210
krypton	211	10	5741.445	6700.326	36.936	27.390	1667.678	137.838
nitrous oxide	311	10	7474.778	13676.531	52.070	50.336	2997.404	185.945
nonane	596	1	2200.687	81692.219	156.217	379.897	715.553	85.318
sulfur dioxide	432	8	8052.256	20821.200	56.819	61.478	4877.456	171.538
toluene	593	3	4186.620	52937.550	105.422	214.488	7705.723	89.464
xenon	291	8	5986.014	9193.668	36.895	28.692	3063.309	125.648
R-116	295	4	3180.336	34509.528	161.389	120.218	2189.730	73.317
R-141b	479	3	4267.596	61757.274	214.894	126.963	1485.482	93.674
R-142b	412	4	4165.652	44982.401	170.029	117.705	3187.214	96.468
R-218	347	3	2742.100	58080.724	251.735	181.131	2375.958	57.554
R-245fa	429	3	3737.844	63909.822	235.875	172.283	1891.958	78.673
R-41[a]	319	9	6130.986	13699.382	55.982	53.388	2724.221	194.624
R-41[b]	319	9	6129.100	13670.133	55.886	55.438	2796.224	189.549

[a] Calculated from eq 14 with coefficients taken from Table 8. [b] Calculated from eq 28.

Conclusions

Short forms for the Helmholtz energy equation of state developed in previous work have been applied to the fluids acetone, carbon monoxide, carbonyl sulfide, decane, hydrogen sulfide, 2-methylbutane (isopentane), 2,2-dimethylpropane (neopentane), 2-methylpentane (isohexane), krypton, nitrous oxide, nonane, sulfur dioxide, toluene, xenon, hexafluoroethane (R-116), 1,1-dichloro-1-fluoroethane (R-141b), 1-chloro-1,1-difluoroethane (R-142b), octafluoropropane (R-218), 1,1,1,3,3-pentafluoropropane (R-245fa), and fluoromethane (R-41). These fluids are available in the Refprop program (Lemmon et al., 2006), which can be used to calculate the thermodynamic and transport properties of many fluids. The applications in this work that were applied to a wide variety of fluids with different polarities demonstrates the ability of the short functional forms to represent the properties of many fluids of industrial interest. To apply the short forms, minimal experimental data are needed. Data are required over a range of temperatures and pressures for at least pressure−density−temperature values and vapor pressure measurements. Additionally, the critical point must be known or estimated, and data should be available in the liquid for the isochoric heat capacity, the isobaric heat capacity, or the speed of sound to verify that the fitted equation properly represents the behavior of derived properties including energies and calorimetric properties. The short form equation of state used here was modified for R-41 by fitting the temperature exponents in addition to the coefficients of the equation to improve the accuracy of calculated fluid properties. As an aid to computer implementation, calculated values of properties from the equations of state are given in Table 10. The number of digits displayed does not indicate the accuracy in the values but is given only for validation of computer code.

At the University of Paderborn in Germany, a research program is underway to develop a new category of short form equations devoted to associating fluids. The following fluids are being considered: inorganic substances (hydrogen chloride, hydrogen fluoride, water, ammonia), alkanols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, 2-pentanol), carboxylic acids (formic acid, acetic acid, propanoic acid, butanoic acid), amines (methylamine, diethylamine), ethers (diethyl ether, dipropyl ether), and halocarbon refrigerants (R-41, R-32, R-40, R-40B1). These families of associating fluids are of great importance for many problems in the process industry. The formation of intermolecular clusters through hydrogen bonds leads to, in comparison with nonpolar or weakly polar fluids, considerable deviations from the behavior in the vapor phase even at low pressures. Both the introduction of physically motivated terms into an empirical equation of state and the development of simultaneously optimized equations of state dedicated to these fluids are being investigated.

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