APPENDIX A

An Equation of State for Pentafluoroethane (HFC-125) for Temperatures from the Triple Point (172.52 K) to 500 K and Pressures to 60 MPa

[manuscript to be submitted to the *Journal of Physical and Chemical Reference Data*]

An Equation of State for Pentafluoroethane (HFC-125) for Temperatures from the Triple Point (172.52 K) to 500 K and Pressures to 60 MPa

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A new formulation is presented for the thermodynamic properties of refrigerant 125 (pentafluoroethane, $\text{CHF}_2\text{-CF}_3$) based upon available experimental data. The formulation can be used for the calculation of all the thermodynamic properties, including density, heat capacity, speed of sound, energy and saturation properties, using an equation of state explicit in Helmholtz energy. Ancillary equations are given for the ideal gas heat capacity, the vapor pressure, and for the saturated liquid and vapor densities as functions of temperature. Comparisons to available experimental data are given that establish the accuracy of calculated properties using this equation of state. The estimated uncertainties of properties calculated using the new equation are 0.1% in density, 0.5% in heat capacities, 0.01% in the speed of sound for the vapor at pressures less than 1 MPa, 0.5% in the speed of sound elsewhere, and 0.1% in vapor pressure. Deviations in the critical region are higher for all properties except vapor pressure. The equation is valid for temperatures from the triple point temperature (172.52 K) to 500 K and pressures up to 60 MPa, and can be extrapolated to 650 K.

Key words: caloric properties; density; equation of state; fundamental equation; HFC-125; R-125; thermodynamic properties; pentafluoroethane.

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List of Symbols

<u>Symbol</u>	<u>Physical quantity</u>	<u>Unit</u>
a	Helmholtz energy	J/mol
B	Second virial coefficient	dm ³ /mol
C	Third virial coefficient	(dm ³ /mol) ²
c_p	Isobaric heat capacity	J/(mol · K)
c_v	Isochoric heat capacity	J/(mol · K)
c_σ	Saturated liquid heat capacity	J/(mol · K)
g	Gibbs energy	J/mol
h	Enthalpy	J/mol
M	Molar mass	g/mol
p	Pressure	MPa
R	Molar gas constant	J/(mol · K)
s	Entropy	J/(mol · K)
T	Temperature	K
u	Internal energy	J/mol
v	Molar volume	dm ³ /mol
w	Speed of sound	m/s
Z	Compressibility factor ($Z = p/\rho RT$)	
α	Reduced Helmholtz energy ($\alpha = a/RT$)	
δ	Reduced density ($\delta = \rho/\rho_c$)	
ϕ	Fugacity coefficient	
ρ	Molar density	mol/dm ³
τ	Inverse reduced temperature ($\tau = T_c/T$)	

Superscripts

0	Ideal gas property
<i>r</i>	Residual
'	Saturated liquid state
"	Saturated vapor state

Subscripts

0	Reference state property
<i>c</i>	Critical point property
calc	Calculated using an equation
data	Experimental value
<i>l</i>	Liquid property
<i>nbp</i>	Normal boiling point property
<i>tp</i>	Triple point property
<i>v</i>	Vapor property
σ	Saturation property

Physical Constants and Characteristic Properties of R-125

<u>Symbol</u>	<u>Quantity</u>	<u>Value</u>
R	Molar gas constant	8.314 472 J/(mol · K)
M	Molar mass	120.0214 g/mol
T_c	Critical temperature	339.173 K
p_c	Critical pressure	3.6177 MPa
ρ_c	Critical density	4.779 mol/dm ³
T_{tp}	Triple point temperature	172.52 K
p_{tp}	Triple point pressure	0.002 914 MPa
ρ_{tpv}	Vapor density at the triple point	0.002 038 mol/dm ³
ρ_{tpl}	Liquid density at the triple point	14.086 mol/dm ³
T_{nbp}	Normal boiling point temperature	225.06 K
ρ_{nbpv}	Vapor density at the normal boiling point	0.056 57 mol/dm ³
ρ_{nbpl}	Liquid density at the normal boiling point	12.611 mol/dm ³
T_0	Reference temperature for ideal gas properties	273.15 K
p_0	Reference pressure for ideal gas properties	0.001 MPa
h_0^0	Reference ideal gas enthalpy at T_0	41266.39 J/mol
s_0^0	Reference ideal gas entropy at T_0 and p_0	236.1195 J/(mol · K)

Introduction

Refrigerant 125 (pentafluoroethane, HFC-125), and commercial blends containing R-125, are leading candidates for replacing the ozone-depleting hydrochlorofluorocarbon R-22 (chlorodifluoromethane, HCFC-22), the production of which will be phased out by the year 2020 under the terms of the Montreal Protocol. The thermodynamic properties of the refrigerant used as the working fluid in a system significantly influence the energy efficiency and capacity of refrigeration equipment, and accurate properties are essential in evaluating potential alternative refrigerants and in designing equipment.

A property formulation is the set of equations used to calculate properties of a fluid at specified thermodynamic states defined by an appropriate number of independent variables. A typical thermodynamic property formulation is based on an equation of state which allows the correlation and computation of all thermodynamic properties of the fluid, including properties such as entropy that cannot be measured directly.

In this work, the general term "equation of state" refers to the empirical models developed for calculating fluid thermodynamic properties. The term "fundamental equation" is often used in the literature to refer to empirical descriptions of one of four fundamental relations: internal energy as a function of volume and entropy, enthalpy as a function of pressure and entropy, Gibbs energy as a function of pressure and temperature, or Helmholtz energy as a function of density and temperature. Modern equations of state for pure fluid properties are usually fundamental equations explicit in the Helmholtz energy as a function of density and temperature. All thermodynamic properties may be calculated without additional ancillary equations for saturation properties through the use of the Maxwell criterion (equal pressures and Gibbs energies at constant temperature during phase changes).

Several equations of state for R-125 have been previously developed by various researchers worldwide. The equation of Sunaga *et al.* (1998) is an 18-term equation explicit in the Helmholtz energy, the equation of Piao and Noguchi (1998) is a 20-term modified Benedict-Webb-Rubin equation, the equation of Outcalt and McLinden (1995) is a 32-term modified Benedict-Webb-Rubin equation, the equation of Ely (1995) is a 27-term equation explicit in Helmholtz energy. The equation of Piao and Noguchi (1998) was selected by Annex 18 of the Heat Pump Programme of the International Energy Agency (IEA) in 1996 as an international

standard formulation for use by the refrigeration industry. The equation of Sunaga *et al.* (1998) became available shortly thereafter, and it has been used as the primary equation for R-125 since that time. Its functional behavior and fit to experimental data are somewhat better than the Piao and Noguchi equation.

The new equation presented here is an 18-term fundamental equation explicit in the reduced Helmholtz energy. This equation represents all the selected experimental data within the estimated experimental uncertainties. To minimize the number of coefficients, the new equation of state for R-125 was developed using state of the art optimization and multi-property fitting algorithms. Other thermodynamic properties are derived from the equation of state by differentiation. The range of validity of the equation of state for R-125 is from the triple point temperature (172.52 K) to 500 K at pressures to 60 MPa. It can be extrapolated to 650 K based on graphical verification of derived properties.

In addition to the equation of state, ancillary functions are given for the vapor pressure and the density of the saturated liquid and saturated vapor. These ancillary equations can be used as initial estimates in computer programs for defining the saturation boundaries, but are not required to calculate properties from the equation of state. Summaries of the available data for the properties of R-125 are given, and the ranges of these data are tabulated.

Vapor-Liquid Coexistence

Critical Point

Critical parameters for R-125 have been reported by various authors and are listed in Table 1. The difficulties in the experimental determination of the critical parameters are the probable cause of considerable differences among the results obtained by the various investigators. The critical density is difficult to determine accurately by experiment because of the infinite compressibility at the critical point and the associated difficulty of reaching thermodynamic equilibrium. Therefore, reported values for the critical density are often calculated by power-law equations, extrapolation of rectilinear diameters using measured saturation densities, or by correlating single-phase data close to the critical point. The critical temperature used in this work was obtained by fitting the data of Kuwabara *et al.* (1995) and Higashi (1994) at temperatures above 324 K to the equation

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

where $T_c = 339.173$ K, $\rho_c = 4.779$ mol/dm³, $N_1 = 0.98136$, $N_2 = 1.9125$, $\beta = 0.33414$, T_{σ} is the saturation temperature, and ρ_{σ} is the saturation density for the liquid or the vapor. The critical density and critical temperature were fitted simultaneously with the coefficients of the equation. Equation (1) is valid only in the critical region. Calculated values from this equation are shown in Figure 1 along with experimental data along the saturation lines, with the lower plot showing a smaller region close to the critical point.

The critical pressure was determined from the equation of state at the critical temperature and density. The resulting values of the critical properties are

$$\begin{aligned} T_c &= 339.173 \text{ K}, \\ \rho_c &= 4.779 \text{ mol/dm}^3, \text{ and} \\ p_c &= 3.6177 \text{ MPa.} \end{aligned} \quad (2)$$

These values should be used for all property calculations from the equation of state. The selected critical temperature agrees well with the values reported by both Kuwabara *et al.* (339.165 K) and Higashi (339.17 K).

Triple Point

The triple point temperature of R-125 was measured by Lüddecke and Magee (1996) by slowly applying a constant heat source to a frozen sample contained within the cell of an adiabatic calorimeter and noting the sharp break in the temperature rise, resulting in

$$T_{tr} = 172.52 \text{ K}, \quad (3)$$

measured on the ITS-90 temperature scale. The value of the triple point pressure calculated from the equation of state given later is 2.914 kPa.

Vapor Pressure

Table 2 summarizes the available vapor pressure data for R-125. The vapor pressure can be represented with the ancillary equation

$$\ln \left(\frac{p_{\sigma}}{p_c} \right) = \frac{T_c}{T} [N_1 \theta + N_2 \theta^{1.5} + N_3 \theta^{2.3} + N_4 \theta^{4.6}], \quad (4)$$

where $N_1 = -7.5295$, $N_2 = 1.9026$, $N_3 = -2.2966$, $N_4 = -3.4480$, $\theta = (1 - T/T_c)$, and p_σ is the vapor pressure. The values of the exponents were determined using non-linear least squares fitting techniques. The values of the critical parameters are given in Eq. (2).

Saturated Densities

Table 3 summarizes the saturated liquid and vapor density data for R-125. The saturated liquid density is represented by the ancillary equation

$$\frac{\rho'}{\rho_c} = 1 + N_1\theta^{1/3} + N_2\theta^{0.6} + N_3\theta^{2.9}, \quad (5)$$

where $N_1 = 1.6684$, $N_2 = 0.88415$, $N_3 = 0.44383$, $\theta = (1 - T/T_c)$, and ρ' is the saturated liquid density.

The saturated vapor density is represented by the equation

$$\ln\left(\frac{\rho''}{\rho_c}\right) = N_1\theta^{0.38} + N_2\theta^{1.22} + N_3\theta^{3.3} + N_4\theta^{6.9}, \quad (6)$$

where $N_1 = -2.8403$, $N_2 = -7.2738$, $N_3 = -21.890$, $N_4 = -58.825$, and ρ'' is the saturated vapor density. Values calculated from the equation of state using the Maxwell criteria were used in developing this equation, and deviations between the equation of state and the ancillary equation are generally less than 0.03% below 337.5 K and less than 0.3% elsewhere. The values of the exponents for equations (5) and (6) were determined using non-linear least squares fitting techniques.

The Equation of State for R-125

The equation of state for R-125 has been formulated using the Helmholtz energy as the fundamental property with independent variables of density and temperature. The equation of state is given by

$$a(\rho, T) = a^0(\rho, T) + a^r(\rho, T), \quad (7)$$

where a 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 which corresponds to the influence of intermolecular forces. All thermodynamic properties can be calculated as derivatives of the Helmholtz energy. For example, the pressure derived from this expression is

$$p = \rho^2 \left(\frac{\partial a}{\partial \rho} \right)_T. \quad (8)$$

The functional form used for the new equation for R-125 is explicit in the dimensionless Helmholtz energy, α , using independent variables of dimensionless density and temperature.

The form of this equation is

$$\frac{a(\rho, T)}{RT} = \alpha(\delta, \tau) = \alpha^0(\delta, \tau) + \alpha^r(\delta, \tau), \quad (9)$$

where $\delta = \rho / \rho_c$, $\tau = T_c / T$, the critical temperature (T_c) is 339.173 K and the critical density (ρ_c) is 4.779 mol/dm³ as given in Eq. (2). The equation for the ideal gas Helmholtz energy is given in the following section and the equation for the residual Helmholtz energy follows the ideal gas section.

Properties of the Ideal Gas

The Helmholtz energy of the ideal gas is given by

$$a^0 = h^0 - RT - Ts^0. \quad (10)$$

The ideal gas enthalpy is given by

$$h^0 = h_0^0 + \int_{T_0}^T c_p^0 dT, \quad (11)$$

where $h_0^0 = 41266.39$ J/mol is the value at $T_0 = 273.15$ K and c_p^0 is the ideal gas heat capacity given by Eq. (15) below. The ideal gas entropy is given by

$$s^0 = s_0^0 + \int_{T_0}^T \frac{c_p^0}{T} dT - R \ln \left(\frac{\rho T}{\rho_0 T_0} \right), \quad (12)$$

where $s_0^0 = 236.1195$ J/(mol · K) is the value for entropy at $T_0 = 273.15$ K and $p_0 = 0.001$ MPa, and ρ_0 is the ideal gas density at T_0 and p_0 , $\rho_0 = p_0 / T_0 R$. The values for h_0^0 and s_0^0 were chosen so that the enthalpy and entropy of the saturated liquid state at 0 °C are 200 kJ/kg and 1 kJ/(kg · K), respectively, corresponding to the common convention in the refrigeration industry. Combining these equations results in the following equation for the Helmholtz energy of the ideal gas,

$$a^0 = h_0^0 + \int_{T_0}^T c_p^0 dT - RT - T \left[s_0^0 + \int_{T_0}^T \frac{c_p^0}{T} dT - R \ln \left(\frac{\rho T}{\rho_0 T_0} \right) \right]. \quad (13)$$

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

$$\alpha^0 = \frac{h_0^0 \tau}{RT_c} - \frac{s_0^0}{R} - 1 + \ln \frac{\delta \tau_0}{\delta_0 \tau} - \frac{\tau}{R} \int_{\tau_0}^{\tau} \frac{c_p^0}{\tau^2} d\tau + \frac{1}{R} \int_{\tau_0}^{\tau} \frac{c_p^0}{\tau} d\tau, \quad (14)$$

where $\delta_0 = \rho_0 / \rho_c$ and $\tau_0 = T_c / T_0$.

In the calculation of the thermodynamic properties of R-125 using an equation of state explicit in the Helmholtz energy, an equation for the ideal gas heat capacity, c_p^0 , is needed to calculate the Helmholtz energy for the ideal gas, α^0 . Values of the ideal gas heat capacity derived from low pressure experimental heat capacity or speed of sound data are given in Table 4 along with theoretical values from statistical methods using fundamental frequencies.

Differences between the different sets of theoretical values arise from the use of different fundamental frequencies and from the models used to calculate the various couplings between the vibrational modes of the molecule. The equation for the ideal gas heat capacity for R-125, used throughout the remainder of this work, was developed by fitting values reported by Yokozeki *et al.* (1998), and is given by

$$\frac{c_p^0}{R} = 3.063T^{0.1} + 2.303 \frac{u_1^2 \exp(u_1)}{[\exp(u_1) - 1]^2} + 5.086 \frac{u_2^2 \exp(u_2)}{[\exp(u_2) - 1]^2} + 7.3 \frac{u_3^2 \exp(u_3)}{[\exp(u_3) - 1]^2}, \quad (15)$$

where u_1 is 314 K/T, u_2 is 756 K/T, u_3 is 1707 K/T and the ideal gas constant, R , is 8.314472 J/(mol · K) (Mohr and Taylor, 1999). The Einstein functions containing the terms u_1 , u_2 , and u_3 were used so that the shape of the ideal gas heat capacity with respect to temperature would be similar to that derived from statistical methods. However, these are empirical coefficients and should not be confused with the fundamental frequencies. Comparisons of values calculated using Eq. (15) to the ideal gas heat capacity data are given in Figure 2. The ideal gas Helmholtz energy equation, derived from Eqs. (14) and (15), is

$$\alpha^0 = \ln \delta - \ln \tau + a_1 + a_2 \tau + a_3 \tau^{-0.1} + a_4 \ln[1 - \exp(-a_5 \tau)] + a_6 \ln[1 - \exp(-a_7 \tau)] + a_8 \ln[1 - \exp(-a_9 \tau)], \quad (16)$$

where $a_1 = 37.2674$, $a_2 = 8.88404$, $a_3 = -49.8651$, $a_4 = 2.303$, $a_5 = -0.92578$, $a_6 = 5.086$, $a_7 = -2.22895$, $a_8 = 7.3$, and $a_9 = -5.03283$.

Properties of the Real Fluid

Unlike the equations for the ideal gas, the real fluid behavior is described using empirical models that are only loosely tied with theoretical techniques. Although it is possible to extract theoretical values such as second and third virial coefficients from the fundamental equation, the

terms in the equation are simply empirical and any connection to theory may not be entirely justified. The coefficients of the equation reported here depend mostly on the experimental data described later.

Selected Database

The units adopted for this work were kelvins (ITS-90) for temperature, MPa for pressure, and mol/dm³ for density. Units of the experimental data were converted as necessary from those of the original publications to these units. Where necessary, temperatures reported on IPTS-68 were converted to the International Temperature Scale of 1990 (ITS-90) (Preston-Thomas, 1990). The ppT and other data selected for the determination of the coefficients of the equation of state are described later along with comparisons of calculated properties to experimental values to verify the accuracy of the model developed in this research. Data used in fitting the equation of state for R-125 were selected to avoid redundancy in various regions of the surface.

Fitting Procedures

The development of the equation of state is a process of correlating selected experimental data by least-squares fitting methods using a model which is generally empirical in nature, but is designed to exhibit proper behavior in the ideal gas and low density regions and to extrapolate to temperatures and pressures higher than those defined by experiment. In all cases, experimental data are considered paramount, and the proof of validity of any equation of state is evidenced in its ability to represent the thermodynamic properties of the fluid within the uncertainty of the experimental values. A secondary test of validity is its ability to extrapolate outside the range of experimental data. The selected data are usually a subset of the available database determined by the correlator to be representative of the most accurate values measured. The type of fitting procedure (*e.g.*, nonlinear versus linear) determines how the experimental data will be used. In this work, a much smaller subset of the most accurate data was used in the nonlinear fitting due to the extensive calculations required to develop the equation. The resulting equation was compared to all experimental data to verify that the data selection had not adversely affected the fit.

Two methods were used to arrive at the final equation of state for R-125. Initial equations were developed using linear regression techniques by fitting ppT data, isochoric heat capacity data, linearized sound speed data, and second virial coefficients, as well as vapor

pressures calculated from the ancillary equation. This process has been widely used to develop equations of state over the last several decades and typically results in equations with 28 to 35 terms. In this work, the best equation developed from the linear regression was used as the starting point for the second method discussed below. Details about the linear regression algorithm can be found elsewhere (Wagner, 1974; Lemmon *et al.*, 2000).

Once a preliminary equation had been developed, nonlinear fitting techniques were used to shorten and improve the equation. Only a subset of the primary data was used. 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. In addition, the exponents for density and temperature, given below in Eq. (17) as i_k , j_k , l_k , and m_k , were also determined simultaneously with the coefficients of the equation. Each data point was individually weighted according to type, region, and uncertainty. The values of the first and second derivatives of pressure with respect to density at the critical point were fitted so that their values would be near zero at the selected critical point given in Eq. (2). To reduce the size of the equation, terms were eliminated by either deleting the term that contributed least to the overall sum of squares or by combining two terms that had similar values of the exponents (resulting in similar contributions to the equation of state). After a term was eliminated, the fit was rerun until the sum of squares with the new equation was of the same magnitude as the previous equation. The final functional form is an equation with 18 terms.

The exponents on density in the equation of state must be integers so that the derivatives of the Helmholtz energy with respect to density have the correct theoretical value (*i.e.*, zero) in the ideal gas limit. Since noninteger values for the density exponents resulted from the nonlinear fitting, a process of rounding a density exponent to the nearest integer, followed by refitting the other parameters to minimize the overall sum of squares, was implemented until all the exponents were integers. A similar process was used for the temperature exponents to reduce the number of significant figures to one or two digits past the decimal point. The final equation with 18 terms represented the experimental data better than preliminary equations resulting from the linear fitter with about 32 terms.

In addition to reducing the number of individual terms in the equation compared to that produced by conventional linear least-squares methods, the extrapolation behavior of the shorter equations is generally more accurate because there are fewer degrees of freedom. In the longer

equations, two or more correlated terms are often needed to reproduce the accuracy of a single term in the nonlinear fit. The values of these correlated terms are often large in magnitude, and their behavior outside the range of validity of the equation is often unreasonable.

Equation for the Residual Helmholtz Energy

The final functional form for the residual Helmholtz energy for R-125 is

$$\alpha^r(\delta, \tau) = \sum_{k=1}^5 N_k \delta^{i_k} \tau^{j_k} + \sum_{k=6}^{15} N_k \delta^{i_k} \tau^{j_k} \exp(-\delta^{l_k}) + \sum_{k=16}^{18} N_k \delta^{i_k} \tau^{j_k} \exp(-\delta^{l_k}) \exp(-\tau^{m_k}). \quad (17)$$

The coefficients N_k of this equation are given in Table 5. The last part of this equation containing the m_k exponents includes new terms developed in this work. These terms drastically minimize the positive and negative pressures calculated using the equation of state along isotherms within the two phase. Although the values of i_k, j_k, l_k , and m_k are arbitrary, j_k , and m_k are generally expected to be greater than zero, and i_k and l_k are integers greater than zero.

The functions used for calculating pressure, compressibility factor, internal energy, enthalpy, entropy, Gibbs energy, isochoric heat capacity, isobaric heat capacity, and the speed of sound from Eq. (9) are given as Eqs. (18-26).

$$p = \rho RT \left[1 + \delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_{\tau} \right] \quad (18)$$

$$Z = \frac{p}{\rho RT} = 1 + \delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_{\tau} \quad (19)$$

$$\frac{u}{RT} = \tau \left[\left(\frac{\partial \alpha^0}{\partial \tau} \right) + \left(\frac{\partial \alpha^r}{\partial \tau} \right)_{\delta} \right] \quad (20)$$

$$\frac{h}{RT} = \tau \left[\left(\frac{\partial \alpha^0}{\partial \tau} \right)_{\delta} + \left(\frac{\partial \alpha^r}{\partial \tau} \right)_{\delta} \right] + \delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_{\tau} + 1 \quad (21)$$

$$\frac{s}{R} = \tau \left[\left(\frac{\partial \alpha^0}{\partial \tau} \right)_{\delta} + \left(\frac{\partial \alpha^r}{\partial \tau} \right)_{\delta} \right] - \alpha^0 - \alpha^r \quad (22)$$

$$\frac{g}{RT} = 1 + \alpha^0 + \alpha^r + \delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_{\tau} \quad (23)$$

$$\frac{c_v}{R} = -\tau^2 \left[\left(\frac{\partial^2 \alpha^0}{\partial \tau^2} \right)_{\delta} + \left(\frac{\partial^2 \alpha^r}{\partial \tau^2} \right)_{\delta} \right] \quad (24)$$

$$\frac{c_p}{R} = \frac{c_v}{R} + \frac{\left[1 + \delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_\tau - \delta \tau \left(\frac{\partial^2 \alpha^r}{\partial \delta \partial \tau} \right)\right]^2}{\left[1 + 2\delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_\tau + \delta^2 \left(\frac{\partial^2 \alpha^r}{\partial \delta^2} \right)_\tau\right]} \quad (25)$$

$$\frac{w^2 M}{RT} = 1 + 2\delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_\tau + \delta^2 \left(\frac{\partial^2 \alpha^r}{\partial \delta^2} \right)_\tau - \frac{\left[1 + \delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_\tau - \delta \tau \frac{\partial^2 \alpha^r}{\partial \delta \partial \tau}\right]^2}{\tau^2 \left[\left(\frac{\partial^2 \alpha^0}{\partial \tau^2} \right)_\delta + \left(\frac{\partial^2 \alpha^r}{\partial \tau^2} \right)_\delta \right]} \quad (26)$$

The fugacity coefficient and second and third virial coefficients are given by Eqs. (27-29).

$$\phi = \exp[Z - 1 - \ln(Z) + \alpha^r] \quad (27)$$

$$B(T) = \frac{1}{\rho_c} \left(\frac{\partial \alpha^r}{\partial \delta} \right)_{\delta=0} \quad (28)$$

$$C(T) = \frac{1}{\rho_c^2} \left(\frac{\partial^2 \alpha^r}{\partial \delta^2} \right)_{\delta=0} \quad (29)$$

Other derived properties, given in Eqs. (30-32), 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 $(\partial p / \partial T)_\rho$.

$$\left(\frac{\partial p}{\partial \rho} \right)_T = RT \left[1 + 2\delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_\tau + \delta^2 \left(\frac{\partial^2 \alpha^r}{\partial \delta^2} \right)_\tau \right] \quad (30)$$

$$\left(\frac{\partial^2 p}{\partial \rho^2} \right)_T = \frac{RT}{\rho} \left[2\delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_\tau + 4\delta^2 \left(\frac{\partial^2 \alpha^r}{\partial \delta^2} \right)_\tau + \delta^3 \left(\frac{\partial^3 \alpha^r}{\partial \delta^3} \right)_\tau \right] \quad (31)$$

$$\left(\frac{\partial p}{\partial T} \right)_\rho = R\rho \left[1 + \delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_\tau - \delta \tau \left(\frac{\partial^2 \alpha^r}{\partial \delta \partial \tau} \right) \right] \quad (32)$$

Equations for additional thermodynamic properties such as the isothermal compressibility and the Joule-Thomson coefficient are given in Lemmon *et al.* (2000).

The derivatives of the ideal gas Helmholtz energy used in the equations above are

$$\begin{aligned} \frac{\partial \alpha^0}{\partial \tau} &= \frac{-1}{\tau} + a_2 - 0.1a_3\tau^{-1.1} \\ &+ a_4a_5 \left[\frac{1}{\exp(a_5\tau)-1} \right] + a_6a_7 \left[\frac{1}{\exp(a_7\tau)-1} \right] + a_8a_9 \left[\frac{1}{\exp(a_9\tau)-1} \right] \end{aligned} \quad (33)$$

and

$$\begin{aligned} \frac{\partial^2 \alpha^0}{\partial \tau^2} &= \tau^{-2} + 0.1(1.1)a_3\tau^{-2.1} \\ &- a_4a_5^2 \frac{\exp(a_5\tau)}{[\exp(a_5\tau)-1]^2} - a_6a_7^2 \frac{\exp(a_7\tau)}{[\exp(a_7\tau)-1]^2} - a_8a_9^2 \frac{\exp(a_9\tau)}{[\exp(a_9\tau)-1]^2} \end{aligned} \quad (34)$$

where a_1 through a_9 are given in Eq. (16). The derivatives of the residual Helmholtz energy are given in Eqs. (35) through (40).

$$\begin{aligned} \frac{\partial \alpha^r}{\partial \delta} &= \sum_{k=1}^5 i_k N_k \delta^{i_k-1} \tau^{j_k} + \sum_{k=6}^{15} N_k \delta^{i_k-1} \tau^{j_k} \exp(-\delta^{l_k}) (i_k - l_k \delta^{l_k}) \\ &+ \sum_{k=16}^{18} N_k \delta^{i_k-1} \tau^{j_k} \exp(-\delta^{l_k}) \exp(-\tau^{m_k}) (i_k - l_k \delta^{l_k}) \end{aligned} \quad (35)$$

$$\begin{aligned} \frac{\partial^2 \alpha^r}{\partial \delta^2} &= \sum_{k=1}^5 i_k (i_k - 1) N_k \delta^{i_k-2} \tau^{j_k} \\ &+ \sum_{k=6}^{15} N_k \delta^{i_k-2} \tau^{j_k} \exp(-\delta^{l_k}) [(i_k - l_k \delta^{l_k}) (i_k - 1 - l_k \delta^{l_k}) - l_k^2 \delta^{l_k}] \\ &+ \sum_{k=16}^{18} N_k \delta^{i_k-2} \tau^{j_k} \exp(-\delta^{l_k}) \exp(-\tau^{m_k}) [(i_k - l_k \delta^{l_k}) (i_k - 1 - l_k \delta^{l_k}) - l_k^2 \delta^{l_k}] \end{aligned} \quad (36)$$

$$\begin{aligned} \frac{\partial^3 \alpha^r}{\partial \delta^3} &= \sum_{k=1}^5 i_k (i_k - 1) (i_k - 2) N_k \delta^{i_k-3} \tau^{j_k} \\ &+ \sum_{k=6}^{15} N_k \delta^{i_k-3} \tau^{j_k} \exp(-\delta^{l_k}) \{ i_k (i_k - 1) (i_k - 2) \\ &+ \delta^{l_k} [-2l_k + 6i_k l_k - 3i_k^2 l_k - 3i_k l_k^2 + 3l_k^2 - l_k^3] + \delta^{2l_k} [3i_k l_k^2 - 3l_k^2 + 3l_k^3] - l_k^3 \delta^{3l_k} \} \\ &+ \sum_{k=16}^{18} N_k \delta^{i_k-3} \tau^{j_k} \exp(-\delta^{l_k}) \exp(-\tau^{m_k}) \{ i_k (i_k - 1) (i_k - 2) \\ &+ \delta^{l_k} [-2l_k + 6i_k l_k - 3i_k^2 l_k - 3i_k l_k^2 + 3l_k^2 - l_k^3] + \delta^{2l_k} [3i_k l_k^2 - 3l_k^2 + 3l_k^3] - l_k^3 \delta^{3l_k} \} \end{aligned} \quad (37)$$

$$\begin{aligned} \frac{\partial \alpha^r}{\partial \tau} &= \sum_{k=1}^5 j_k N_k \delta^{i_k} \tau^{j_k-1} + \sum_{k=6}^{15} j_k N_k \delta^{i_k} \tau^{j_k-1} \exp(-\delta^{l_k}) \\ &+ \sum_{k=16}^{18} N_k \delta^{i_k} \tau^{j_k-1} \exp(-\delta^{l_k}) \exp(-\tau^{m_k}) (j_k - m_k \tau^{m_k}) \end{aligned} \quad (38)$$

$$\frac{\partial^2 \alpha^r}{\partial \tau^2} = \sum_{k=1}^5 j_k (j_k - 1) N_k \delta^{i_k} \tau^{j_k - 2} + \sum_{k=6}^{15} j_k (j_k - 1) N_k \delta^{i_k} \tau^{j_k - 2} \exp(-\delta^{l_k}) \\ + \sum_{k=16}^{18} N_k \delta^{i_k} \tau^{j_k - 2} \exp(-\delta^{l_k}) \exp(-\tau^{m_k}) \left[(j_k - m_k \tau^{m_k}) (j_k - 1 - m_k \tau^{m_k}) - m_k^2 \tau^{m_k} \right] \quad (39)$$

$$\frac{\partial^2 \alpha^r}{\partial \tau \partial \delta} = \sum_{k=1}^5 i_k j_k N_k \delta^{i_k - 1} \tau^{j_k - 1} + \sum_{k=6}^{15} j_k N_k \delta^{i_k - 1} \tau^{j_k - 1} \exp(-\delta^{l_k}) (i_k - l_k \delta^{l_k}) \\ + \sum_{k=16}^{18} j_k N_k \delta^{i_k - 1} \tau^{j_k - 1} \exp(-\delta^{l_k}) \exp(-\tau^{m_k}) (i_k - l_k \delta^{l_k}) (j_k - m_k \tau^{m_k}) \quad (40)$$

Experimental Data and Comparisons to the Equation of State

During the last several years, many experimental studies of the thermodynamic properties of R-125 have been reported, *e.g.*, ppT properties, saturation properties, critical parameters, heat capacities, speeds of sound, second virial coefficients, and ideal gas heat capacities. Selected data were used for the development of the new thermodynamic property formulation reported here. Comparisons were made to all available experimental data, including those not used in the development of the equation of state.

The accuracy of the equation of state was determined by statistical comparisons of property values calculated using the equation of state to experimental data. These statistics are based on the percent deviation in any property, X , defined as

$$\% \Delta X = 100 \left(\frac{X_{\text{data}} - X_{\text{calc}}}{X_{\text{data}}} \right). \quad (41)$$

Using this definition, the average absolute deviation is defined as

$$\text{AAD} = \frac{1}{n} \sum_{i=1}^n |\% \Delta X_i|, \quad (42)$$

where n is the number of data points. The average absolute deviations between experimental data and the equation of state are given in the tables summarizing the data. In Tables 2 and 3, measured properties are compared with the equation of state, not with the ancillary equations. The comparisons given in the sections below for the various datasets compare values from the equation of state to the experimental data using the average absolute deviation as given by Equation (42). Discussions of maximum errors or of systematic offsets use the absolute values of the deviations.

Comparisons with Saturation Data

Figure 3 shows comparisons of vapor pressures calculated from the equation of state with experimental data. The dashed lines in these figures represent the ancillary equation, Eq. (4). The maximum deviation between the vapor pressure ancillary equation and the equation of state is 0.03%. When calculating vapor pressures from the equation of state (not from the ancillary equations), the average deviations are less than 0.1% for the datasets of Baroncini *et al.* (1993), Boyes and Weber (1995), de Vries (1997), Duarte-Garza and Magee (1997), Gorenflo *et al.* (1996), Monluc *et al.* (1991), Oguchi *et al.* (1996), Sagawa *et al.* (1994), Weber and Silva (1994), and Ye *et al.* (1995). Comparisons with the equation of Sunaga *et al.* (1998) are also shown in Figure 3. Their equation is very similar to that presented here at temperatures above 250 K, but tends to follow the data of de Vries (1997) at lower temperatures. The data of de Vries show different trends at low temperatures than those of Duarte-Garza and Magee and of Weber and Silva. The Duarte-Garza and Magee values are derived from caloric information in the two-phase region; they agree well with the data of Weber and Silva measured with ebulliometer techniques (with a small offset of 0.05%). In a similar fashion to the outcome of the IEA-Annex for R-143a (see Lemmon and Jacobsen, 2000), the vapor pressure values of Duarte-Garza and Magee (1997) were believed to be the most reliable values available at low temperatures. However, the estimated uncertainty of the model must be large enough to include the data from all these various sources.

Figure 4 shows comparisons of saturated liquid densities calculated from the equation of state with experimental data. All data are fitted well with increasing deviations as the critical region is approached. This region is shown in Figure 5, displaying both saturated liquid and vapor densities in the critical region. There are no saturated vapor density data outside the critical region. The dashed lines in these figures represent the ancillary equations reported in Eqs. (5) and (6). In the critical region, the equation of state agrees well with the data of Kuwabara *et al.* (1995) and Higashi (1994), with increasing deviations as the critical point is approached (between 4 and 5 mol/dm³). Near a density of 6 mol/dm³, the equation shows an offset of about 1% with the data of Kuwabara *et al.* However, the power law equation used to represent these and other critical region data showed the same tendency as the equation of state, even though fitted with completely different parameters and input data. Although not entirely conclusive, this behavior supports the decision made by the authors in representing the saturation

properties for R-125. The model favors the data of Higashi (1994) but the uncertainty of calculated values must include the values of Kuwabara *et al.* (1995).

***ppT* Data and Virial Coefficients**

The experimental *ppT* data for R-125 are summarized in Table 6 and shown graphically in Figure 6. For clarity, data in the critical region are also shown in Figure 7. Figure 8 shows comparisons of densities calculated from the equation of state with experimental data and Figure 9 shows comparisons of pressures calculated from the equation of state with the experimental data in the extended critical region of R-125. In these figures, data of a given type are separated into temperature increments of 10 K outside the critical region; the temperatures listed at the top of each small plot are the lower bounds of the data in the plot, and the comparisons to the equation of state of Sunaga *et al.* are given at this temperature.

Below 270 K, the equation of state represents the data of Magee (1996), Duarte-Garza *et al.* (1997), and de Vries (1997) with deviations in density generally less than 0.05%. Between 270 and 330 K in the liquid, density deviations are slightly higher for the data of Duarte-Garza *et al.* and Perkins (2002), and somewhat lower (0.02%) for the data of de Vries and for Defibaugh and Morrison (1992). In the vapor phase up to 330 K, the datasets are not as consistent as are those in the liquid, and density deviations tend to be higher, except for the data of de Vries which is represented by an AAD of 0.018%. Deviations for other datasets in this region are 0.12% for Zhang *et al.* (1996), 0.08% for Boyes and Weber (1995), and 0.17% for Ye *et al.* (1995). Omitting the data in the region between 3 and 7 mol/dm³ and at temperatures up to 360 K (*i.e.*, the critical region), the spread in the data at higher temperatures continues to increase, and the deviations remain under 0.1% for only the datasets of de Vries, Zhang *et al.*, Ye *et al.*, Boyes and Weber, Magee, and Perkins. Of particular interest in this region are the data of Perkins, with more than 1200 data points spanning pressures up to 20 MPa and temperatures up to 429 K. Deviations of density values calculated using the equation of state from these data are about 0.04% in this region.

In the critical region omitted above, from 3 to 7 mol/dm³ with temperatures to 360 K, deviations in density are no longer a useful comparison. Comparisons of calculated values with even the most accurate data show average deviations of 0.4% (de Vries) and 0.85% (Perkins) with maximum errors exceeding 5% in density. In order to compare the equation of state against experimental data in this region, deviations in pressure are more meaningful and the following

discussion uses this statistic. Figure 9 shows comparisons of values from the equation to data in a limited region around the critical point. Most of the data in this region are represented with average deviations of 0.1%. The scatter in the data tends to be fairly similar for most of the datasets with deviations of calculated values from the data of de Vries of about 0.06%. Average deviations for comparisons with other datasets are 0.19% for Perkins, 0.27% for Sagawa *et al.* (1994), and 0.31% for Defibaugh and Morrison. The maximum deviation from the data of de Vries is 0.22%.

Table 7 summarizes the sources for the second virial coefficients of R-125. Additional values for the second virial coefficient were numerically determined by fitting $(Z-1)/\rho$ as a function of density using the data of de Vries (1997). The additional data are shown in Figure 10 as circles. These values are given in Table 8. Data below 0.1 mol/dm^3 were not used since such low density data may be subject to larger errors due to local adsorption onto the walls of the apparatus or to higher uncertainties in the measurement of extremely low pressures. The solid lines show isotherms calculated from the equation of state presented here and the solid curve represents the saturated vapor density. The y-intercept (zero density) represents the second virial coefficient at a given temperature, and the third virial coefficient can be taken from the slope of each line at zero density. The values of the second virial coefficient calculated from the equation of state (the values of the lines in the figure at zero density) agree well with those determined numerically and shown as circles in the figure. Comparisons of second virial coefficients calculated with the equation of state and those determined from the data of de Vries (given in Table 8) are shown in Figure 11. The uncertainty in the derived values at lower temperatures is higher due to the limited data at densities above 0.1 mol/dm^3 and to the higher curvature in the data (unlike higher temperatures where the data can be fit to a straight line). Figure 11 shows comparisons with other reported second virial coefficients as well, showing good agreement between the equation of state and the values reported by de Vries (1997), Gillis (1997), and Grigante *et al.* (2000). Differences tend to be slightly larger around 320 to 350 K, however, the equation of Sunaga *et al.* (1998) shows the same trends.

Caloric Data

The sources of experimental data for the speed of sound of R-125 are summarized in Table 9 and shown graphically in Figure 12. Comparisons of values calculated from the equation

of state for the speed of sound are shown in Figure 13 for the vapor phase and in Figure 14 for the liquid phase. The equation represents the vapor phase data of Gillis (1997) and Ichikawa *et al.* (1998) within 0.01% and the liquid phase data of Takagi (1996) within 0.3%. There are no speed of sound data below 240 K, however, the extrapolation behavior is quite reasonable at low temperatures as discussed below.

The reported measurements of the isochoric heat capacity, saturated liquid heat capacity, and isobaric heat capacity for R-125 are summarized in Table 10 and also illustrated in Figure 12. Comparisons of values calculated from the equation of state are shown for the isochoric heat capacities in Figure 15, saturated liquid heat capacities in Figure 16, and isobaric heat capacities in Figure 17. Lüddecke and Magee (1998b) measured both the isochoric heat capacity of R-125 and the heat capacity along the saturated liquid line. The average deviation between values from the equation of state and these data is 0.57% for the isochoric heat capacity and 0.24% for the saturated liquid heat capacity. There is little information concerning the isobaric heat capacity of R-125, especially in the vapor phase (five points by Wilson *et al.*, 1992), and the data in the liquid phase are not consistent. Although none of these data were used in the fit, the equation of state represents the data of Gunther and Steimle (1997) within 0.5%. This agreement indicates consistency between the fitted isochoric and saturated heat capacity data of Lüddecke and Magee and the isobaric heat capacity data of Gunther and Steimle.

Extrapolation Behavior

Plots of certain characteristic curves are useful in assessing the behavior of an equation of state in regions away from the available data (Deiters and de Reuck, 1997, Span and Wagner, 1997, Span, 2000). The characteristic curves considered in this work are the Boyle curve, given by the equation

$$\left(\frac{\partial Z}{\partial v} \right)_T = 0, \quad (43)$$

the Joule-Thomson inversion curve,

$$\left(\frac{\partial Z}{\partial T} \right)_p = 0, \quad (44)$$

the Joule Inversion curve,

$$\left(\frac{\partial Z}{\partial T}\right)_v = 0, \quad (45)$$

and the ideal curve,

$$\frac{p}{\rho RT} = 1. \quad (46)$$

These characteristic curves for the equation of state for R-125 are illustrated in Figure 18. Although the curves in this figure do not provide numerical information, the reasonable shapes of these curves as shown indicate qualitatively correct extrapolation behavior of the equation of state extending to extremely high pressures and temperatures far in excess of the likely thermal stability of the fluid.

Plots of constant property lines on various thermodynamic coordinates are useful in assessing the behavior of the equation of state. The equation developed here was used to produce plots of temperature versus isochoric heat capacity (Figure 19), isobaric heat capacity (Figure 20), and speed of sound (Figure 21). These plots indicate that the equation of state exhibits reasonable behavior over all temperatures and pressures within the range of validity and that the extrapolation behavior is reasonable at higher temperatures and pressures. Figure 22 verifies that the equation of state extrapolates to extremely high temperatures and pressures, however, much of this diagram is well above the region where R-125 dissociates, and these regions are shown only to illustrate the well behaved nature of the equation.

Estimated Uncertainty of Calculated Properties

The new reference equation of state describes the $p\rho T$ surface with an uncertainty of 0.1% in density at temperatures from the triple point to 500 K and pressures up to 60 MPa, except in the critical region where an uncertainty of 0.1% in pressure is generally attained. At temperatures below 330 K, the uncertainty in density in the liquid phase may be as low as 0.02%. In the gaseous and supercritical region, speed of sound data are represented within 0.01% at pressures below 1 MPa. The estimated uncertainty for heat capacities is 0.5% and the estimated uncertainty for the speed of sound in the liquid phase is 0.5% for $T > 250$ K. The saturation values can be calculated from the equation of state by application of the Maxwell criterion, which requires equal Gibbs energies and equal pressures for saturated liquid and vapor states at the

same temperature. The estimated uncertainties of vapor pressures and saturated liquid densities calculated using the Maxwell criterion are 0.1% for each property, and the estimated uncertainty for saturated vapor density is 0.2%. In the critical region, the uncertainty for the densities increases. Based on graphical verification of the derived properties, the equation can be extended to 650 K with estimated uncertainties of 0.2% in density and 1.0% in heat capacities and sound speeds.

Acknowledgments

This work was funded by the 21-CR research program of the Air-Conditioning and Refrigeration Technology Institute; the Office of Building Technology, State and Community Programs of the U.S. Department of Energy; and by NIST. We thank Dr. Mark McLinden of NIST, Boulder, for his assistance and suggestions during the development and documentation of the equation.

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Table 1. Summary of critical point parameters

Author	Critical Temp. (K)	Critical Pressure (MPa)	Critical Density (kg/m ³)	Critical Density (mol/dm ³)
Duarte-Garza <i>et al.</i> (1997)	339.41	3.6391	572.26	4.768
Fukushima and Ohotoshi (1992)	339.18	3.621	562.	4.6825
Higashi (1994)	339.17	3.62	572.	4.7658
Kuwabara <i>et al.</i> (1995)	339.165		568.	4.7325
Nagel and Bier (1993)	339.43	3.635	568.	4.7325
Schmidt and Moldover (1994)	339.33		565.	4.7075
Singh <i>et al.</i> (1991)	339.45	3.6428	570.98	4.7573
Wilson <i>et al.</i> (1992)	339.1725	3.595	571.3	4.7600
Values adopted in this work	339.173	3.6177		4.779

Table 2. Summary of vapor pressure data

Author	No. of Points	Temp. Range (K)	AAD (%)
Baroncini <i>et al.</i> (1993)	58	235-333	0.062
Boyes and Weber (1995)	29	273-335	0.019
de Vries (1997)	98	222-339	0.030
Duarte-Garza <i>et al.</i> (1997)	15	220-337	0.204
Duarte-Garza and Magee (1997)	12	172-225	0.038
Gorenflo <i>et al.</i> (1996)	25	233-337	0.061
Lee <i>et al.</i> (2000)	3	293-313	0.167
Lüddecke and Magee (1996)	8	180-250	0.285
Magee (1996)	34	180-335	0.209
Monluc <i>et al.</i> (1991)	23	303-339	0.056
Nagel and Bier (1993)	18	205-339	0.521
Oguchi <i>et al.</i> (1996)	61	223-338	0.081
Sagawa (1994)	23	313-339	0.080
Sagawa <i>et al.</i> (1994)	26	308-339	0.042
Tsvetkov <i>et al.</i> (1995)	34	263-338	0.055
Weber and Silva (1994)	114	175-284	0.027
Widiatmo <i>et al.</i> (1994)	20	219-334	0.324
Wilson <i>et al.</i> (1992)	39	195-339	0.451
Ye <i>et al.</i> (1995)	12	290-339	0.070

Table 3. Summary of saturated liquid and vapor density data

Author	No. of Points	Temp. Range (K)	AAD (%)
Saturated liquid density data			
Defibaugh and Morrison (1992)	9	275-337	0.376
Higashi (1994)	9	324-339	0.830
Kuwabara <i>et al.</i> (1995)	16	331-339	1.313
Magee (1996)	7	173-308	0.102
Widiatmo <i>et al.</i> (1994)	25	219-334	0.076
Saturated vapor density data			
Higashi (1994)	8	326-339	0.752
Kuwabara <i>et al.</i> (1995)	13	335-339	1.748

Table 4. Summary of ideal gas heat capacity data

Author	No. of Points	Temp. Range (K)	AAD (%)
Experimental Data			
Gillis (1997)	8	240-380	0.067
Grigianti <i>et al.</i> (2000)	7	260-360	0.153
Hozumi <i>et al.</i> (1996)	6	273-343	0.799
Theoretical Values			
Chen <i>et al.</i> (1975)	18	100-1500	0.860
Yokozeiki <i>et al.</i> (1998)	45	120-1000	0.014

Table 5. Parameters and coefficients of the equation of state

k	N_k	i_k	j_k	l_k	m_k
1	5.280760	1	0.669		
2	-8.676580	1	1.05		
3	0.7501127	1	2.75		
4	0.7590023	2	0.956		
5	0.01451899	4	1.00		
6	4.777189	1	2.00	1	
7	-3.330988	1	2.75	1	
8	3.775673	2	2.38	1	
9	-2.290919	2	3.37	1	
10	0.8888268	3	3.47	1	
11	-0.6234864	4	2.63	1	
12	-0.04127263	5	3.45	1	
13	-0.08455389	1	0.72	2	
14	-0.1308752	5	4.23	2	
15	0.008344962	1	0.20	3	
16	-1.532005	2	4.5	2	1.7
17	-0.05883649	3	29.0	3	7.0
18	0.02296658	5	24.0	3	6.0

Table 6. Summary of ppT data

Source	No. of Points	Temp. Range (K)	Pressure Range (MPa)	Density Range (mol/dm ³)	AAD (%)
Baroncini <i>et al.</i> (1993)	58	0.99-2.52	0.50-1.29	293-338	0.389
Boyes and Weber (1995)	92	0.33-4.56	0.12-2.83	273-363	0.056
de Vries (1997)	962	0.02-19.8	0.01-12.6	243-413	0.072
Defibaugh and Morrison (1992)	162	1.59-6.33	2.15-11.2	275-369	0.697
Duarte-Garza <i>et al.</i> (1997)	148	1.24-67.9	7.62-14.2	180-350	0.089
Magee (1996)	77	3.58-35.4	9.29-14.0	178-398	0.034
Monluc <i>et al.</i> (1991)	50	1.57-11.1	0.81-7.83	310-423	0.700
Oguchi <i>et al.</i> (1996)	167	0.81-17.0	0.42-9.54	280-473	0.956
Perkins (2002)	1483	2.88-19.7	3.13-9.96	301-428	0.105
Sagawa <i>et al.</i> (1994)	211	0.69-11.8	0.30-8.87	308-423	0.977
Takahashi <i>et al.</i> (1999)	131	0.10-8.40	0.03-4.77	298-423	0.513
Tsvetkov <i>et al.</i> (1995)	44	0.60-6.09	0.30-4.31	273-443	0.799
Wilson <i>et al.</i> (1992)	84	1.73-10.4	0.89-13.6	198-448	1.382
Ye <i>et al.</i> (1995)	93	0.12-3.55	0.04-1.91	290-390	0.115
Zhang <i>et al.</i> (1996)	93	0.12-3.55	0.04-1.91	290-390	0.075

Table 7. Summary of second virial coefficients

Author	No. of Points	Temp. Range (K)	AAD ^a (cm ³ /mol)
Bignell and Dunlop (1993)	3	290-310	1.006
Boyes and Weber (1995)	8	280-350	2.342
de Vries (1997) ^b	19	263-413	1.436
Gillis (1997)	9	240-400	1.914
Grigianti <i>et al.</i> (2000)	7	260-360	0.934
Ye <i>et al.</i> (1995)	11	290-390	6.397
Zhang <i>et al.</i> (1995)	11	290-390	2.599

^aAverage absolute difference in the second virial coefficient (cm³/mol)^bData were derived from the *ppT* data of de Vries and are given in Table 8.Table 8. Second virial coefficients derived from the *ppT* data of de Vries (1997)

Temp. (K)	B (dm ³ /mol)	Temp. (K)	B (dm ³ /mol)
263.150	-0.4984	339.152	-0.2677
273.150	-0.4560	340.150	-0.2672
283.151	-0.4180	341.153	-0.2648
293.151	-0.3850	343.152	-0.2603
303.150	-0.3529	346.152	-0.2548
313.150	-0.3269	353.150	-0.2426
323.150	-0.3028	363.152	-0.2254
333.150	-0.2808	373.152	-0.2095
335.150	-0.2766	393.150	-0.1837
337.151	-0.2722	413.152	-0.1603

Table 9. Summary of speed of sound data

Author	No. of Points	Temp. Range (K)	Pressure Range (MPa)	AAD (%)
Vapor phase data				
Hozumi <i>et al.</i> (1996)	72	273-343	0.01-0.24	0.034
Ichikawa <i>et al.</i>	74	273-343	0.01-0.50	0.007
Grigianti <i>et al.</i> (2000)	69	260-360	0.05-0.50	0.019
Gillis (1997)	149	240-400	0.04-1.02	0.008
Liquid phase and saturation data				
Grebenkov <i>et al.</i> (1994)	30	288-333	1.14-16.4	0.233
Kraft and Leipertz (1994)	13	293-338	Sat. liq.	2.211
Kraft and Leipertz (1994)	9	307-338	Sat. vap.	1.560
Takagi (1996)	167	241-333	0.23-32.2	0.264

Table 10. Summary of experimental heat capacity data

Author	No. of Points	Temp. Range (K)	Density Range (mol/dm ³)	Pressure Range (MPa)	AAD (%)
Isochoric heat capacity data					
Perkins (2002)	474	305-397		4.00-19.5	1.185
Lüddecke and Magee (1996)	99	200-342	10.5-13.5		0.577
Saturated heat capacity data					
Lüddecke and Magee (1996)	93	176-278			0.244
Isobaric heat capacity data					
Kan <i>et al.</i> (1996)	78	276-328		1.59-3.04	1.820
Wilson <i>et al.</i> (1992)	10	216-333		0.13-3.45	1.182
Gunther and Steimle (1996)	24	203-318		Sat. liq.	0.520

Figure 1. Critical region saturation data.

Figure 2. Comparisons of ideal gas heat capacities calculated with the ancillary equation to experimental and theoretical data.

Figure 3. Comparisons of vapor pressures calculated with the equation of state to experimental data.

Figure 4. Comparisons of saturated liquid densities calculated with the equation of state to experimental data.

Figure 5. Comparisons of saturated liquid and vapor densities in the critical region calculated with the equation of state to experimental data.

Figure 6. Experimental $p\rho T$ data.

Figure 7. Experimental ppT data in the critical region.

Figure 8. Comparisons of densities calculated with the equation of state to experimental data.

Figure 8. Comparisons of densities calculated with the equation of state to experimental data (continued).

+ Baroncini <i>et al.</i> (1993)	× Boyes and Weber (1995)
□ de Vries (1997)	○ Defibaugh and Morrison (1992)
* Duarte-Garza <i>et al.</i> (1997)	▷ Magee (1996)
△ Monluc <i>et al.</i> (1991)	△ Oguchi <i>et al.</i> (1996)
▽ Perkins (2002)	^ Sagawa <i>et al.</i> (1994)
< Tsvetkov <i>et al.</i> (1995)	◄ Wilson <i>et al.</i> (1992)
→ Ye <i>et al.</i> (1995)	↗ Zhang <i>et al.</i> (1996)
— Sunaga <i>et al.</i> (1998)	

Figure 9. Comparisons of pressures calculated with the equation of state to experimental data in the critical region.

Figure 10. Derivation of second virial coefficients from the $p\rho T$ data of de Vries (1997).

Figure 11. Comparisons of second virial coefficients calculated with the equation of state to experimental data.

Figure 13. Comparisons of speeds of sound in the vapor phase calculated with the equation of state to experimental data.

Figure 14. Comparisons of speeds of sound in the liquid phase calculated with the equation of state to experimental data.

Figure 15. Comparisons of isochoric heat capacities calculated with the equation of state to experimental data.

◁ Lueddecke and Magee (1996)

Figure 16. Comparisons of saturated heat capacities calculated with the equation of state to experimental data.

Figure 17. Comparisons of isobaric heat capacities calculated with the equation of state to experimental data.

Figure 18. Characteristic curves of the equation of state.

Figure 19. Isochoric heat capacity versus temperature diagram.

Figure 20. Isobaric heat capacity versus temperature diagram.

Figure 21. Speed of sound versus temperature diagram.

Figure 22. Pressure versus density diagram showing extrapolation behavior to extreme conditions.

APPENDIX - Tables of Thermodynamic Properties of R-125

Thermodynamic Properties of R-125 at Saturation (even increments of temperature)

T °C	p MPa	ρ kg/m ³	h kJ/kg	s kJ/(kg K)	c_v kJ/(kg K)	c_p kJ/(kg K)	w m/s
-100.630	0.00291	1690.7 0.24462	87.130 277.39	.49022 1.5931	0.6776 0.4984	1.035 0.5689	932.6 116.4
-100.	0.00309	1688.7 0.25834	87.782 277.74	.49399 1.5911	0.6781 0.4997	1.035 0.5703	929.2 116.6
-95.	0.00481	1672.5 0.39179	92.969 280.54	.52352 1.5764	0.6818 0.5099	1.040 0.5810	903.2 118.0
-90.	0.00729	1656.2 0.57794	98.181 283.36	.55236 1.5634	0.6860 0.5201	1.045 0.5919	877.5 119.4
-85.	0.01074	1639.9 0.83142	103.42 286.20	.58059 1.5520	0.6906 0.5304	1.051 0.6031	852.3 120.7
-80.	0.01547	1623.4 1.1691	108.70 289.06	.60824 1.5421	0.6955 0.5409	1.058 0.6146	827.5 121.9
-75.	0.02179	1606.7 1.6103	114.01 291.94	.63537 1.5333	0.7006 0.5514	1.066 0.6264	802.9 123.1
-70.	0.03008	1589.9 2.1766	119.36 294.83	.66201 1.5257	0.7060 0.5620	1.074 0.6385	778.6 124.1
-65.	0.04076	1572.9 2.8921	124.75 297.71	.68821 1.5191	0.7115 0.5727	1.082 0.6511	754.5 125.1
-60.	0.05432	1555.7 3.7833	130.19 300.60	.71398 1.5135	0.7171 0.5836	1.091 0.6641	730.6 126.0
-55.	0.07126	1538.2 4.8791	135.68 303.48	.73937 1.5086	0.7229 0.5946	1.101 0.6776	706.8 126.8
-50.	0.09216	1520.5 6.2112	141.21 306.35	.76439 1.5044	0.7288 0.6058	1.111 0.6916	683.2 127.4
-45.	0.11763	1502.4 7.8140	146.80 309.20	.78907 1.5009	0.7349 0.6171	1.121 0.7063	659.6 127.9
-40.	0.14830	1484.0 9.7249	152.44 312.03	.81345 1.4980	0.7410 0.6286	1.132 0.7216	636.1 128.3
-35.	0.18487	1465.3 11.985	158.14 314.84	.83753 1.4955	0.7473 0.6402	1.144 0.7376	612.6 128.6
-30.	0.22806	1446.1 14.639	163.90 317.61	.86135 1.4935	0.7537 0.6520	1.157 0.7545	589.1 128.7
-25.	0.27861	1426.5 17.736	169.73 320.34	.88493 1.4919	0.7602 0.6640	1.170 0.7724	565.7 128.7
-20.	0.33733	1406.4 21.331	175.62 323.03	.90829 1.4906	0.7668 0.6761	1.184 0.7912	542.2 128.5
-15.	0.40501	1385.8 25.486	181.59 325.67	.93145 1.4895	0.7736 0.6882	1.199 0.8112	518.7 128.1
-10.	0.48252	1364.5 30.271	187.64 328.24	.95443 1.4887	0.7805 0.7003	1.216 0.8324	495.2 127.5
-5.	0.57072	1342.6 35.768	193.77 330.74	.97728 1.4881	0.7876 0.7122	1.234 0.8550	471.6 126.8
0.	0.67052	1319.8 42.070	200.00 333.16	1.0000 1.4875	0.7948 0.7240	1.255 0.8797	448.0 125.8

Thermodynamic Properties of R-125 at Saturation (even increments of temperature)

T °C	p MPa	ρ kg/m ³	h kJ/kg	s kJ/(kg K)	c_v kJ/(kg K)	c_p kJ/(kg K)	w m/s
5.	0.78288	1296.2 49.291	206.33 335.47	1.0226 1.4869	0.8021 0.7359	1.277 0.9073	424.3 124.6
10.	0.90875	1271.5 57.564	212.76 337.66	1.0452 1.4863	0.8095 0.7483	1.303 0.9392	400.4 123.2
15.	1.04918	1245.6 67.054	219.32 339.71	1.0678 1.4856	0.8172 0.7617	1.332 0.9770	376.3 121.5
20.	1.20520	1218.3 77.966	226.02 341.58	1.0904 1.4846	0.8252 0.7764	1.367 1.023	352.0 119.6
25.	1.37792	1189.4 90.557	232.87 343.26	1.1131 1.4834	0.8335 0.7928	1.407 1.080	327.4 117.3
30.	1.56853	1158.4 105.17	239.91 344.71	1.1359 1.4817	0.8425 0.8111	1.457 1.152	302.4 114.8
35.	1.77827	1125.0 122.27	247.16 345.88	1.1591 1.4794	0.8522 0.8315	1.521 1.245	276.9 111.9
40.	2.00849	1088.4 142.52	254.67 346.69	1.1826 1.4764	0.8630 0.8542	1.605 1.372	250.8 108.6
45.	2.26074	1047.7 166.95	262.52 347.05	1.2067 1.4724	0.8755 0.8796	1.724 1.553	223.8 104.8
50.	2.53680	1001.1 197.29	270.83 346.75	1.2318 1.4667	0.8907 0.9083	1.910 1.842	195.6 100.5
55.	2.83891	945.35 236.92	279.83 345.44	1.2585 1.4584	0.9106 0.9421	2.252 2.386	165.3 95.6
60.	3.17028	872.09 294.37	290.10 342.21	1.2884 1.4448	0.9411 0.9856	3.139 3.833	131.5 89.8
65.	3.53697	735.11 416.57	304.88 332.24	1.3311 1.4120	1.014 1.060	13.67 20.07	90.0 82.6
66.	3.61607	612.97 534.59	314.86 321.41	1.3602 1.3795	1.078 1.093	818.2 923.0	78.9 79.2
66.023	3.61770	573.58	318.06	1.3696			

Thermodynamic Properties of R-125 at Saturation (even increments of pressure)

T °C	p MPa	ρ kg/m ³	h kJ/kg	s kJ/(kg K)	c_v kJ/(kg K)	c_p kJ/(kg K)	w m/s
-100.630	0.00291	1690.7	87.130	.49022	0.6776	1.035	932.6
		0.24462	277.39	1.5931	0.4984	0.5689	116.4
-76.278	0.02	1611.0	112.65	.62849	0.6993	1.064	809.2
		1.4866	291.20	1.5355	0.5487	0.6233	122.8
-65.319	0.04	1574.0	124.41	.68655	0.7111	1.082	756.1
		2.8415	297.53	1.5195	0.5721	0.6503	125.0
-58.200	0.06	1549.4	132.16	.72316	0.7192	1.095	722.0
		4.1526	301.64	1.5116	0.5876	0.6689	126.3
-52.785	0.08	1530.4	138.12	.75049	0.7255	1.105	696.3
		5.4381	304.75	1.5067	0.5996	0.6837	127.1
-48.356	0.10	1514.6	143.04	.77254	0.7308	1.114	675.4
		6.7064	307.29	1.5032	0.6095	0.6964	127.6
-48.089	0.101325	1513.6	143.34	.77386	0.7311	1.115	674.2
		6.7900	307.44	1.5030	0.6101	0.6971	127.6
-39.747	0.15	1483.1	152.73	.81467	0.7413	1.133	634.9
		9.8304	312.18	1.4978	0.6292	0.7224	128.4
-33.154	0.20	1458.3	160.26	.84635	0.7496	1.149	603.9
		12.916	315.87	1.4947	0.6446	0.7438	128.7
-27.735	0.25	1437.3	166.53	.87206	0.7566	1.162	578.5
		15.984	318.85	1.4927	0.6574	0.7625	128.7
-23.093	0.30	1418.9	171.97	.89386	0.7627	1.175	556.7
		19.045	321.37	1.4913	0.6686	0.7795	128.6
-19.009	0.35	1402.4	176.80	.91289	0.7681	1.187	537.6
		22.108	323.56	1.4904	0.6785	0.7951	128.4
-15.347	0.40	1387.3	181.18	.92984	0.7731	1.198	520.4
		25.178	325.49	1.4896	0.6874	0.8098	128.1
-12.018	0.45	1373.2	185.19	.94518	0.7777	1.209	504.7
		28.259	327.21	1.4890	0.6954	0.8237	127.8
-8.957	0.50	1360.0	188.91	.95921	0.7820	1.220	490.3
		31.356	328.77	1.4886	0.7028	0.8370	127.4
-6.119	0.55	1347.6	192.39	.97217	0.7860	1.230	476.9
		34.471	330.19	1.4882	0.7095	0.8498	127.0
-3.469	0.60	1335.7	195.67	.98424	0.7898	1.240	464.4
		37.607	331.49	1.4879	0.7158	0.8623	126.5
-0.980	0.65	1324.3	198.77	.99555	0.7933	1.251	452.6
		40.766	332.69	1.4876	0.7217	0.8747	126.0
1.369	0.70	1313.4	201.72	1.0062	0.7967	1.261	441.5
		43.951	333.80	1.4873	0.7272	0.8869	125.5
3.596	0.75	1302.9	204.54	1.0163	0.8000	1.271	431.0
		47.163	334.83	1.4871	0.7325	0.8992	125.0
5.714	0.80	1292.7	207.24	1.0259	0.8031	1.281	420.9
		50.404	335.79	1.4869	0.7377	0.9116	124.4
7.735	0.85	1282.8	209.83	1.0350	0.8061	1.291	411.2
		53.677	336.68	1.4866	0.7426	0.9242	123.8

Thermodynamic Properties of R-125 at Saturation (even increments of pressure)

T °C	p MPa	ρ kg/m ³	h kJ/kg	s kJ/(kg K)	c_v kJ/(kg K)	c_p kJ/(kg K)	w m/s
9.670	0.90	1273.1 56.982	212.33 337.52	1.0437 1.4864	0.8090 0.7475	1.301 0.9370	402.0 123.3
11.525	0.95	1263.7 60.321	214.75 338.30	1.0521 1.4861	0.8118 0.7523	1.311 0.9500	393.1 122.7
13.309	1.00	1254.5 63.697	217.09 339.03	1.0602 1.4858	0.8146 0.7570	1.322 0.9635	384.5 122.1
16.686	1.10	1236.6 70.564	221.56 340.36	1.0754 1.4853	0.8198 0.7665	1.343 0.9915	368.1 120.9
19.841	1.20	1219.2 77.596	225.80 341.53	1.0897 1.4847	0.8249 0.7759	1.365 1.021	352.8 119.6
22.806	1.30	1202.3 84.806	229.84 342.55	1.1031 1.4839	0.8298 0.7854	1.389 1.053	338.2 118.3
25.605	1.40	1185.7 92.209	233.71 343.45	1.1158 1.4832	0.8346 0.7949	1.413 1.088	324.4 117.0
28.258	1.50	1169.4 99.823	237.43 344.24	1.1280 1.4823	0.8393 0.8045	1.439 1.125	311.1 115.7
30.781	1.60	1153.4 107.66	241.02 344.91	1.1395 1.4814	0.8439 0.8141	1.466 1.165	298.4 114.3
33.189	1.70	1137.4 115.75	244.50 345.49	1.1507 1.4803	0.8486 0.8238	1.496 1.208	286.2 113.0
35.492	1.80	1121.5 124.11	247.88 345.98	1.1614 1.4792	0.8532 0.8336	1.528 1.256	274.3 111.6
39.823	2.00	1089.8 141.74	254.40 346.67	1.1817 1.4766	0.8626 0.8534	1.602 1.366	251.7 108.7
43.837	2.20	1057.6 160.82	260.66 347.01	1.2010 1.4734	0.8724 0.8734	1.692 1.504	230.2 105.7
47.578	2.40	1024.5 181.71	266.74 346.99	1.2195 1.4697	0.8829 0.8939	1.809 1.684	209.4 102.7
51.084	2.60	989.96 204.93	272.71 346.57	1.2374 1.4652	0.8945 0.9151	1.966 1.930	189.2 99.5
54.381	2.80	952.95 231.31	278.66 345.68	1.2550 1.4596	0.9077 0.9375	2.194 2.294	169.2 96.2
57.490	3.00	912.04 262.29	284.72 344.18	1.2728 1.4526	0.9237 0.9620	2.565 2.893	149.1 92.8
60.426	3.20	864.39 300.75	291.08 341.78	1.2912 1.4432	0.9446 0.9901	3.288 4.077	128.4 89.3
63.198	3.40	802.42 354.37	298.28 337.68	1.3120 1.4292	0.9757 1.026	5.402 7.502	106.5 85.6
65.800	3.60	668.27 480.94	310.49 326.28	1.3474 1.3940	1.052 1.085	71.10 95.87	81.4 80.5
66.023	3.6177	573.58	318.06	1.3696			