

Equation of State for the Thermodynamic Properties of 1,1,2,2,3-Pentafluoropropane (R-245ca)

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Abstract An equation of state for the calculation of the thermodynamic properties of 1,1,2,2,3-pentafluoropropane (R-245ca), which is a hydrofluorocarbon refrigerant, is presented. The equation of state (EOS) is expressed in terms of the Helmholtz energy as a function of temperature and density, and can calculate all thermodynamic properties through the use of derivatives of the Helmholtz energy. The equation is valid for all liquid, vapor, and supercritical states of the fluid, and is valid from the triple point to 450 K, with pressures up to 10 MPa. Comparisons to experimental data are given to verify the stated uncertainties in the EOS. The estimated uncertainty for density is 0.1 % in the liquid phase between 243 K and 373 K with pressures up to 6.5 MPa; the uncertainties increase outside this range, and are unknown. The uncertainty in vapor-phase speed of sound is 0.1 %. The uncertainty in vapor pressure is 0.2 % between 270 K and 393 K. The uncertainties in other regions and properties are unknown due to a lack of experimental data.

Keywords Equation of state \cdot Helmholtz energy \cdot R-245ca \cdot Thermodynamic properties \cdot 1,1,2,2,3-Pentafluoropropane

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1 Introduction

R-245ca or 1,1,2,2,3-pentafluoropropane (CHF₂ – CF₂ – CH₂F) is a potential replacement for refrigerants in chillers and other cooling cycles, and can be used in organic Rankine cycle applications [1]. R-245ca has zero ozone depletion potential (ODP), and a global warming potential (GWP) of 693 over a 100-year time horizon (carbon dioxide's GWP is defined as 1.0) [1]. Even though it is slightly flammable, blends of R-245ca with other refrigerants may not be flammable.

Experimental data from the literature were used to develop a fundamental equation of state that is valid over the entire fluid surface and that can be used to calculate all of the thermodynamic properties. The experimental values were reported in references [2–7] and are summarized in Table 1. The present equation of state is compatible with the NIST REFPROP database (Lemmon et al. [8]), and can be used in the design of refrigeration or thermal systems that use R-245ca.

There are many publications dealing with the type of equation of state presented in this work; see, for example, the publication of Lemmon et al. [9] for propane. The details given here about the functional form are very limited, providing only the most basic equations. Other sources, e.g. [9], should be consulted to obtain additional details that are not covered here.

Reference	No. points	Temp. Range (T/K)	Pressure range (<i>p</i> /MPa)	Density range $(\rho/\text{mol}\cdot\text{dm}^{-3})$	AAD (%)
Vapor pressures					
Defibaugh et al. [3]	58	298-392	0.1-1.4		0.048
Di Nicola and Passerini [5]	39	258-353	0.016-0.573		0.391
Single-phase densities					
Defibaugh et al. [3]	285	243-372	1-6.5	8.84-11.4	0.009
Di Nicola and Passerini [5]	34	334–364	0.301-0.55	0.119-0.208	1.06
Saturated liquid densities					
Defibaugh et al. [3]	29	243-372		8.78-11.3	0.009
Beyerlein et al. [2]	6	295-413		7.36-10	2.46
Calculated vapor densities					
Defibaugh et al. [3]	32	243-400		0.003-0.712	0.95
Ideal-gas heat capacities					
Gillis [6]	5	311-400			0.178
Isobaric heat capacities					
Hwang et al. [7]	1	313	9.9-10.2		3.47
Speeds of sound					
Gillis [6]	84	311-400	0.051-0.876		0.043
Second virial coefficients					
Gillis [6]	5	311-400			0.31

Table 1 Summary and comparisons of experimental data for R-245ca

2 Critical and Fixed Point Parameters

Defibaugh et al. [3] reported a critical temperature of 447.57 K, a critical pressure of 3.925 MPa, and a critical density of 523.6 kg·m⁻³ (\approx 3.906 mol·dm⁻³). The critical density used in this work was fitted simultaneously with the other parameters in the equation of state, and is based on molar units. The critical pressure was calculated from the critical temperature and density after the equation was finalized. The critical point values for this work are

$$T_{\rm c} = 447.57$$
 K,
 $p_{\rm c} = 3.9407$ MPa, and
 $\rho_{\rm c} = 3.92$ mol·dm⁻³ (≈ 525.468 kg·m⁻³).

Di Nicola et al. [4] measured the triple-point temperature and reported values of 196.0 K and 195.7 K. The value of 196.0 K was selected in this work for the lower-temperature limit of the equation. Calculated values from the equation of state give a triple-point pressure of 0.12 kPa, and saturated liquid and vapor density values of 12.13 mol·dm⁻³ and 0.000073 mol·dm⁻³. The molar mass of R-245ca is 134.04794 g·mol⁻¹, and the value of the gas constant is 8.3144621 J·mol⁻¹·K⁻¹. The acentric factor is 0.355.

3 Ancillary Equations for the Saturation Properties

The boundaries between liquid and vapor are defined by saturation states, and ancillary equations can be used to give good estimates. These ancillary equations are not required when a full equation of state is available, since application of the Maxwell criteria to the equation of state can yield the saturation states [9]. The ancillary equations can be used to give estimates for the pressure and densities required in the iterative procedure to find the saturation states.

The vapor pressure can be represented with the ancillary equation

$$\ln\left(\frac{p_{\sigma}}{p_{c}}\right) = \frac{T_{c}}{T} \left[N_{1}\theta + N_{2}\theta^{1.5} + N_{3}\theta^{2.6} + N_{4}\theta^{5.2} \right],\tag{1}$$

where $N_1 = -7.8757$, $N_2 = 2.0426$, $N_3 = -3.3614$, $N_4 = -4.8567$, $\theta = (1 - T/T_c)$, and p_{σ} is the vapor pressure. The values for the critical points of the ancillary equations are given in the previous section. The saturated-liquid density can be represented by the ancillary equation

$$\frac{\rho'}{\rho_{\rm c}} = 1 + N_1 \theta^{0.48} + N_2 \theta + N_3 \theta^{1.6} + N_4 \theta^{2.4} + N_5 \theta^{3.5},\tag{2}$$

where $N_1 = 4.0075$, $N_2 = -4.6786$, $N_3 = 6.6575$, $N_4 = -5.096$, $N_5 = 2.364$, $\theta = (1 - T/T_c)$, and ρ' is the saturated liquid density. The saturated vapor density can be represented by the equation

$$\ln\left(\frac{\rho''}{\rho_{\rm c}}\right) = N_1 \theta^{0.505} + N_2 \theta^{1.65} + N_3 \theta^{2.5} + N_4 \theta^{5.5} + N_5 \theta^{12},\tag{3}$$

where $N_1 = -4.8138$, $N_2 = -5.557$, $N_3 = -11.257$, $N_4 = -55.775$, $N_5 = -138.45$, and ρ'' is the saturated vapor density.

The ancillary equations were developed by fitting calculated saturation values obtained through the use of the Maxwell criteria applied to the equation of state. Values calculated from these ancillary equations and the equation of state agree to within ± 0.03 %. Very close to the critical point (less than 1 K), the maximum deviation is 0.2 % in the density equations.

4 Equation of State

The only equation of state available prior to the one presented here is an extended corresponding states (ECS) equation with R-134a as a reference fluid; the structure of this prior equation is given by Huber and Ely [10]. Both the ECS model and the Helmholtz energy equation presented here fitted essentially the same data sets.

The Helmholtz energy form of the equation of state is the most widely used method for calculating thermodynamic properties with low uncertainties, as given by

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

where *a* is the Helmholtz energy, α^0 (δ , τ) is the reduced ideal-gas contribution to the Helmholtz energy, and α^r (δ , τ) is the reduced residual Helmholtz energy. The independent variables in the functional form are the reduced density and temperature, $\delta = \rho/\rho_c$ and $\tau = T_c/T$. All thermodynamic properties can be calculated as derivatives of the Helmholtz energy; for example, the pressure derived from this expression is

$$p = \rho^2 \left(\frac{\partial a}{\partial \rho}\right)_T.$$
(5)

The reduced ideal-gas Helmholtz energy equation is

$$\alpha^{0} = a_{1} + a_{2}\tau + \ln \delta + (c_{0} - 1) \ln \tau + \sum_{k=1}^{3} v_{k} \ln \left[1 - \exp \left(-u_{k}\tau / T_{c} \right) \right], \quad (6)$$

where $a_1 = -18.09410031$ and $a_2 = 8.996084665$ correspond to an enthalpy and entropy of 200 kJ·kg⁻¹ and 1 kJ·kg⁻¹·K⁻¹, respectively, for the saturated liquid state at 0 °C. The values of the other constants are $c_0 = 8.888$, $v_1 = 0.8843$, $v_2 = 14.46$, $v_3 = 5.331$, $u_1 = 865$ K, $u_2 = 1122$ K, and $u_3 = 2830$ K, with a molar gas constant *R* of 8.3144621 J·mol⁻¹·K⁻¹.

The constants for the ideal-gas Helmholtz energy were derived from the equation for the ideal-gas heat capacity

k	N _k	t _k	d_k	l_k	η_k	β_k	γ_k	ε_k
1	0.04489247	1	4					
2	1.526476	0.26	1					
3	-2.408320	1	1					
4	-0.5288088	1.2	2					
5	0.18222346	0.67	3					
6	-1.063228	1.92	1	2				
7	-0.2231490	2	3	2				
8	1.187380	1.5	2	1				
9	-0.9772383	1.93	2	2				
10	-0.02296938	1.06	7	1				
11	1.364444	0.17	1		1.16	2.4	1.265	0.55
12	-0.5080666	3.9	1		1.1	1.5	0.42	0.724
13	-0.06649496	1	3		1.64	4.2	0.864	0.524
14	-1.128359	1	3		13.8	379	1.15	0.857

 Table 2
 Coefficients of the equation of state

$$\frac{c_p^0}{R} = c_0 + \sum_{k=1}^3 v_k \left(\frac{u_k}{T}\right)^2 \frac{\exp\left(u_k/T\right)}{\left[\exp\left(u_k/T\right) - 1\right]^2},\tag{7}$$

where the coefficients are identical to those above. These parameters were fitted to the ideal-gas heat capacity values reported by Gillis [6] simultaneously with the residual part of the equation of state.

The functional form for the residual Helmholtz energy equation used for the properties of R-245ca is

$$\alpha^{\mathbf{r}}(\delta,\tau) = \sum_{k=1}^{5} N_k \delta^{d_k} \tau^{t_k} + \sum_{k=6}^{10} N_k \delta^{d_k} \tau^{t_k} \exp\left(-\delta^{l_k}\right) + \sum_{k=11}^{14} N_k \delta^{d_k} \tau^{t_k} \exp\left(-\eta_k \left(\delta - \varepsilon_k\right)^2 - \beta_k \left(\tau - \gamma_k\right)^2\right)$$
(8)

The coefficients and exponents of the residual part of the equation of state are given in Table 2. The Helmholtz energy equation of state, and the fitting process is described in detail by Lemmon et al. [9, 11]; these papers also describe the calculation of other thermodynamic properties from the Helmholtz energy.

5 Comparisons to Experimental Data

The comparisons between experimental data and calculated values are used to estimate the uncertainties in the equation of state, 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

$$\%\Delta X = 100 \left(\frac{X_{\exp} - X_{calc}}{X_{\exp}}\right),\tag{9}$$

and the average absolute deviation is defined as

$$AAD = \frac{1}{n} \sum_{i=1}^{n} |\% \Delta X_i|, \qquad (10)$$

where n is the number of data points. The AAD between experimental data and the equation of state are given in Table 1 summarizing the data.

Only two sets of experimental data for the vapor pressure of R-245ca are available. Comparisons of the equation of state are shown in Fig. 1. The data of Defibaugh et al. [3] span the range from 298 K to 392 K, and are represented by the equation with an AAD of 0.048 %. The bias between these data and the equation is quite small, except at lower temperatures where the equation deviates from the three experimental data points at 298 K by 0.03 %, 0.16 %, and 0.32 %. The data of Di Nicola and Passerini [5] cover the region from 258 K to 353 K, and the equation represents these data with an AAD of 0.4 %. Above 273 K, the equation shows a bias ranging from 0.07 % to 0.7 %; between 263 K and 273 K the equation differs from the five data points at 258 K and 260 K are about -1 %. It is not clear if there is a discontinuity in the data at 275 K, or if the equation has the wrong curvature at lower temperatures. The scatter diagram in the publication of Di Nicola and Passerini shows a similar trend at 275 K, but is not discussed. In the region of overlap between these data and the data of Defibaugh



Fig. 1 Relative deviations of experimental vapor pressures for R-245ca from values calculated with the equation of state



Fig. 2 Relative deviations of experimental single-phase densities for R-245ca from values calculated with the equation of state

et al., there is a difference of about 0.5 % at the lower temperatures, but the latter data do not extend to low enough temperatures to determine the source of the differences.

There are three data sets for the densities of R-245ca. As shown in Fig. 2, the equation of state deviates from the liquid-phase data of Defibaugh et al. [3] by less than ± 0.025 % in density, except for 4 data points at 372 K that deviate by -0.05 %. The authors did not give the uncertainty in their reported values, but measurements from their lab of densities of other fluids typically have uncertainties less than 0.1 %.

Defibuugh et al. extrapolated their single-phase liquid data to the saturation line for each isotherm, and the equation of state represents these data within ± 0.03 %. They used the principle of a linear rectilinear diameter to predict saturated vapor-phase values from the saturated liquid-phase data. At the lowest temperatures, the vapor-phase densities are too small to report a percent deviation. For example, at the lowest temperature of 243 K, the value of $0.00317 \text{ mol}\cdot\text{dm}^{-3}$ from the equation of state is very close to their predicted value of $0.00331 \text{ mol}\cdot\text{dm}^{-3}$. Deviations range from near 0.07 % at 320 K to 0.5 % at their highest measured temperature (372 K). They extrapolated three additional temperatures up to 400 K, but the equation deviates significantly from these points (2.4 %). Deviations between our equation and these data are not shown in the figures. Through the use of the multi-property fitting algorithms applied to both data and constraints in our work, calculated values from the equation of state in the vapor phase most likely represent the actual fluid properties with lower uncertainties.

In the vapor phase, the deviations of the density data from Di Nicola and Passerini [5] deviate on average by about 1 %, with all data points higher than the equation of state. This offset in the vapor is caused by fitting the speed of sound data of Gillis [6]. Different fits were tried that fitted both sets together, then each separately. By themselves, the data of a particular set could be fitted quite well, with the other showing considerable offsets. Fitting the two sets together was not possible. The final equation represents a compromise between the two data sets, weighted more toward the speed of sound data, which show a systematic offset of up to 0.1 % as shown in Fig. 3, while the density data show a systematic offset of up to 1 %. A diagram in the publication of Di Nicola and Passerini shows a similar trend and confirms this discrepancy. Additionally,



Fig. 3 Relative deviations of experimental speeds of sound for R-245ca from values calculated with the equation of state

the calculated vapor-phase densities from Defibaugh et al. [3] (which were not fitted) are better represented by the equation of state when the speed of sound data are favored.

Gillis [6] derived second virial coefficients from his measured speed of sound data. The largest deviation from the equation is $2.5 \text{ dm}^3 \cdot \text{mol}^{-1}$, and the average absolute deviation is 0.31 %. Hwang et al. [7] measured the isobaric heat capacity in the liquid phase at 313 K; the equation deviates from this point by 3.5 %, which is close to the uncertainty reported by the authors.

6 Extrapolation Behavior

Plots of various properties are useful to establish the extrapolation behavior of an equation of state. Many recent publications, including those given in references [11, 12], show the proper behavior of an equation at low and high temperatures, and at high densities and pressures. The behavior of the proposed equation is quite similar as shown in those plots and is not shown here; however, the REFPROP software [8] can be used to generate the diagrams for inspection of the extrapolation behavior.

Some new criteria are now available for evaluating equations of state, in particular is the phase identification parameter (PIP) defined by Venkatarathnam and Oellrich [13], and shown in Fig. 4 for R-245ca. This property is more sensitive than other properties, such as heat capacities and speeds of sound, and can be used to visualize deficiencies in an equation of state. The work of Lemmon et al. [14] describes how this parameter should behave outside the region of validity for an equation of state. In Fig. 5, the PIP is plotted against temperature, with lines of constant pressure along with the saturated liquid curve. Temperature is plotted on a log scale to help visualize the characteristics of the equation. The PIP shows negative curvature between 0.01 K and 10 K. At lower temperatures, the curvature is positive, but with an incorrect negative slope at the lowest temperatures. As shown in Fig. 6, between 200 K and 300 K, the PIP shows some characteristics often seen in the recent development of other equations of state, that being less curvature than at higher temperatures or between 100 K and 200 K. This behavior is still being investigated, with the governing principle that



Fig. 4 Phase identification parameter versus temperature of R-245ca for the full surface. States are shown along the saturation lines and along isobars ranging from 0.5 MPa to 8 MPa with steps of 0.5 MPa



Fig. 5 Phase identification parameter versus temperature of R-245ca at low temperatures in the liquid phase. States are shown along the saturation lines and along isobars ranging from 0.5 MPa to 8 MPa with steps of 0.5 MPa

all derivatives of the PIP with respect to temperature should be positive along the saturated liquid line.

Although investigating the equation at such extremely low temperatures has no significance on the properties of a real fluid, it demonstrates that the extrapolation behavior of the equation below the triple-point temperature is much better than that calculated with older equations of state. This is very important in mixtures where



Fig. 6 Phase identification parameter versus temperature of R-245ca in the liquid region. States are shown along the saturation lines and along isobars ranging from 0.5 MPa to 8 MPa with steps of 0.5 MPa

equations are often used below their triple points to calculate valid liquid states. The ability of the equation to extrapolate so well is achieved through the use of very low temperature exponents for the polynomial terms and the simple exponential terms in the functional form (terms one through ten in Eq. 8). The largest exponent in this equation has a value of two. Higher values increase the rate at which properties change at low temperatures. The work of Lemmon and Jacobsen [11] on the development of an equation for R-125 demonstrates some of the extreme behavior that can be seen in works from many years ago. The publication of Thol and Lemmon [15] on R-1234ze(E) shows similar well-behaved characteristics as with R-245ca, along with additional plots of the PIP and a discussion of the behavior demonstrated by that equation of state.

7 Conclusions

We have presented an equation of state for R-245ca that can be used to evaluate this fluid in refrigeration and thermal applications. Very few data sets are available, and additional data are required to improve the fit. In particular, values of the heat capacities at saturation in the liquid phase and measurements of the speed of sound in the liquid phase are needed, along with density data in the near critical region. No data are currently available below 240 K, and lower-temperature data of all property types would be desirable if low-temperature applications were anticipated for this fluid. Measurements at high temperatures and pressures would require further investigation of the stability of R-245ca with respect to thermal degradation and polymerization, but the present data should be adequate for most applications.

Т (К)	ρ (mol·dm ⁻³)	p (MPa)	c_v (J·mol ⁻¹ ·K ⁻¹)	c_p (J·mol ⁻¹ ·K ⁻¹)	$w (m \cdot s^{-1})$
				, , , , , , , , , , , , , , , , , , , ,	
250	11.3	7.998072	127.995	176.671	971.213
400	8.0	2.017058	151.601	226.229	326.167
448	3.92	3.970007	189.859	23758.6	73.1890
250	0.0	0.0	96.4517	104.766	129.781
420	1.0	2.282553	155.316	218.413	112.579
450	7.0	8.304540	160.706	237.245	256.123

Table 3 Calculated values of properties from the equation of state to verify computer code

Calculated values of properties in the liquid, vapor, and supercritical regions from the equation of state are given in Table 3 and can be used to validate computer code generated with the equations and coefficients given in this work. The number of significant digits does not represent the uncertainty in the data, but are given as an aid for code verification. The state point at zero density can be used to test the ideal-gas properties. The state at 448 K is very close to the critical point, where the properties of the fluid change rapidly. Calculations that are identical to those given in the table for this point will demonstrate the correct implementation of the model.

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