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Application of Nonlinear Regression in the Development of a Wide Range Formulation for HCFC-22[1]

A. Kamei,[2] S. W. Beyerlein,[2,3] and R. T Jacobsen[2]

An equation of state has been developed for HCFC-22 for temperatures from the triple point (115.73 K) to 550 K, at pressures up to 60 MPa. Based on comparisons between experimental data and calculated properties, the accuracy of the wide-range equation of state is $\pm 0.1\%$ in density, $\pm 0.3\%$ in speed of sound, and $\pm 1.0\%$ in isobaric heat capacity, except in the critical region. Nonlinear fitting techniques were used to fit a liquid equation of state based on P–ρ–T, speed of sound, and isobaric heat capacity data. Properties calculated from the liquid equation of state were then used to expand the range of validity of the wide range equation of state for HCFC-22.

KEY WORDS: chlorodifluoromethane; equation of state; HCFC-22; nonlinear fitting; thermodynamic properties.

1. INTRODUCTION

HCFC-22 (chlorodifluoromethane; $CHClF_2$), although ultimately destinated to be phased out, is expected to be used as a working fluid in energy systems such as heat pumps for the next 25 years. HCFC-22 has one of the largest experimental databases of the refrigerants. For this reason, McLinden and Didion [1] have noted that HCFC-22 may be a good reference fluid for developing corresponding states methods for predicting properties of alternative refrigerants. Kamei et al. [2] reported a wide-range equation of state applicable from 200 to 550 K at pressures up to 60 MPa. This correlation was developed using linear regression.

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[2] Center for Applied Thermodynamic Studies, University of Idaho, Moscow, Idaho 83844-1011, U.S.A.

[3] To whom correspondence should be addressed.

The work described here extends the lower temperature limit of the equation of state reported by Kamei et al. [2] from 200 K to the triple point (115.73 K). This improvement was made possible through application of nonlinear techniques. A method developed by Powell [3] was used to correlate thermodynamic property data in the liquid region. Numerical pseudo-data calculated from the liquid-region equation of state were incorporated in the development of a new wide-range equation of state for HCFC-22. A detailed discussion of the new wide-range equation of state is presented elsewhere [4, 5].

2. FUNDAMENTAL EQUATION OF STATE

The functional form of the equation of state is based on a fundamental equation explicit in reduced Helmholtz energy,

$$\alpha(\delta, \tau) = \frac{A(\rho, T)}{RT} = \alpha^0(\delta, \tau) + \bar{\alpha}(\delta, \tau) \qquad (1)$$

The independent variables for this equation are reduced density ($\delta = \rho/\rho_c$) and reciprocal reduced temperature ($\tau = T_c/T$), where ρ_c is the critical density and T_c is the critical temperature. The term α^0 is the dimensionless ideal gas Helmholtz energy,

$$\alpha^0(\delta, \tau) = \frac{H_0^0 \tau}{RT_c} - \frac{S_0^0}{R} - 1 + \ln \frac{\delta \tau_0}{\delta_0 \tau} - \frac{\tau}{R} \int_{\tau_0}^{\tau} \frac{C_p^0}{\tau^2} \, d\tau + \frac{1}{R} \int_{\tau_0}^{\tau} \frac{C_p^0}{\tau} \, d\tau \qquad (2)$$

where $\delta_0 = \rho_0/\rho_c$ and $\tau_0 = T_c/T_0$. The value of ρ_0 is calculated as the ideal gas density at $T_0 = 273.15$ K and $P_0 = 0.001$ MPa. The datum state values for enthalpy and entropy are $H_0^0 = 35874.80\ \text{J} \cdot \text{mol}^{-1}$ and $S_0^0 = 205.2925\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. These values were selected such that the saturated liquid values of enthalpy and entropy at 0°C are $200\ \text{kJ} \cdot \text{kg}^{-1}$ and $1.0\ \text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$, respectively. The molecular weight of HCFC-22 is $86.469\ \text{g} \cdot \text{mol}^{-1}$ and the universal gas constant, R, used in this work is $8.31451\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. The ideal gas heat capacity equation for C_p^0 is given as

$$\frac{C_p^0}{R} = 4 + \sum_{k=1}^{9} \frac{u_k^2 \exp(u_k)}{(\exp(u_k) - 1)^2} + B_{10} + B_{11} T \qquad (3)$$

where $u_k = B_k/T$. Coefficients for Eq. (3) are given in Table I. The term $\bar{\alpha}$ is the contribution to the dimensionless Helmholtz energy due to compressibility,

$$\bar{\alpha}(\delta, \tau) = \sum_{k=1}^{m} N_k \delta^{i_k} \tau^{j_k} \exp(-\gamma \delta^{l_k}) \qquad (4)$$

Table I. Coefficients of Ideal Gas Heat Capacity Eq. (4) for HCFC-22

$B_1 = 4352.3095$
$B_2 = 1935.1591$
$B_3 = 1887.67936$
$B_4 = 1694.88284$
$B_5 = 1605.67848$
$B_6 = 1162.53424$
$B_7 = 857.51288$
$B_8 = 605.72638$
$B_9 = 530.90982$
$B_{10} = 5.26140446 \times 10^{-3}$
$B_{11} = 1.20662553 \times 10^{-4}$

Here m is the number of terms in the equation, the N_k are the coefficients of the equation of state, $\gamma = 0$ for terms with $l_k = 0$, and $\gamma = 1$ for terms with l_k greater than zero. Values of N_k, i_k, j_k, and l_k are determined by fitting an equation of state to experimental data.

Comparisons of calculated properties to experimental data are widely used as the basis for estimating the accuracy of equations of state. Equation (5) defines the average absolute deviation (AAD) for a property of interest, Y.

$$\%\,\mathrm{AAD} = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{Y_i^{\mathrm{exp}} - Y_i^{\mathrm{cal}}}{Y_i^{\mathrm{exp}}} \right| \times 100 \tag{5}$$

In this equation, the superscript "exp" represents experimental data, the superscript "cal" represents a property calculated from the equation of state, and n is the number of data points.

3. EXPERIMENTAL DATA FOR FCFC-22

The critical temperature (369.295 K) and the critical pressure (4.990 MPa) reported by Higashi et al. [6] were adopted in this study. The liquid-volume fraction method of Van Poolen [7] was used to determine the critical density ($6.05822\ \mathrm{mol \cdot dm^{-3}}$). All temperature values were converted to the International Temperature Scale of 1990 (ITS-90).

An extensive set of experimental P–ρ–T data is available from 120 to 523 K, at pressures up to 160 MPa. In the liquid region below 200 K, Händel et al. [8] and Blanke and Weiss [9] reported the most accurate and extensive P–ρ–T data sets. Kohlen et al. [10], Michels [11], Oguchi et al. [12], and Zander [13] presented accurate P–ρ–T data sets at temperatures above 200 K in the liquid and vapor regions. Niepmann et al. [14] reported extensive speed of sound data (w–P–T) which cover the liquid region from 200 to 300 K, up to 60 MPa. Blanke and Weiss [9] also reported speed of sound data in the vapor region. No isochoric heat capacity data are available for HCFC-22 in the liquid region. This makes it difficult to develop an accurate equaion of state in the liquid region by linear regression. The only reliable isobaric heat capacity data (C_p–P–T) in the liquid region are by Neilson and White [15]. These data are located along the saturated liquid line at temperatures from 121 to 226 K. In the vapor region, the most accurate isobaric heat capacity data sets are reported by Tanishita et al. [16], Ernst and Busser [17], and Bier et al. [18].

4. DEVELOPMENT OF A NEW WIDE-RANGE FORMULATION FOR HCFC-22

The procedure used to develop the new equation of state for HCFC-22 consisted of (i) defining a preliminary equation of state in the liquid region; (ii) applying nonlinear regression in the liquid region, (iii) incorporating the results of nonlinear regression in developing a wide-range equation of state using linear regression; and (iv) evaluating the accuracy of the wide-range equation of state. Figure 1 gives a flowchart of this procedure.

4.1. Preliminary Equation of State for the Liquid Region

P–ρ–T, w–ρ–T, and C_v–ρ–T data sets were calculated from a previous equation of state [2] (referred to as the original equation in this work) and used along with experimental measurements to develop a preliminary equation of state in the liquid region. These data sets covered temperatures from 150 to 350 K at pressures up to 60 MPa. Each data set contained 217 data points.

The preliminary liquid-region equation of state was developed using multiproperty, stepwise linear regression. The generated data sets were weighted by the uncertainties listed in Table II. This procedure resulted in a preliminary equation which is nearly as accurate as the original wide-range equation of state [2] in the liquid region. The range of validity of this equation is 180 to 350 K.

Table II. Uncertainties Used in the Error Propagation Calculation of Least-Squares Weights

Property	P	ρ	T	w	C_v
Uncertainty	0.01 %	0.1 %	2 mK	0.1 %	0.5 %

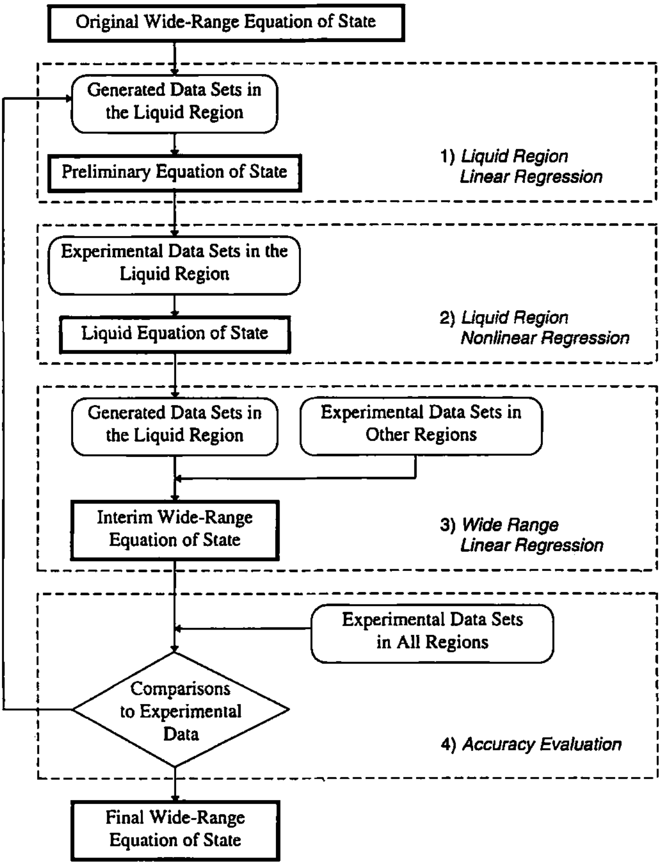

Fig. 1. Procedure for developing a wide-range equation of state.

4.2. Nonlinear Regression in the Liquid Region

Along with experimental measurements, P–ρ–T data generated from the original equation of state were used in the nonlinear regression since the data of Händel et al. [8] showed systematic density deviations of 0.05% compared to data of Blanke and Weiss [9]. Speed sound data by Niepmann et al. [14] cover temperatures from 200 to 300 K. At temperatures from 150 to 250 K, speed-of-sound values along the saturated liquid line were calculated by extrapolating the ancillary equation (w'–T) of Niepmann et al. [14].

The coefficients of the real gas part of the Helmholtz energy, N_k, in the preliminary equation of state were optimized using nonlinear regression. Equation (6) shows the objective function which was minimized in the nonlinear regression.

$$
\begin{aligned}
S = {} & \frac{10^{-7}}{n_P} \sum_{i=1}^{n_P} \left(\frac{P_i^{\exp} - P_i^{\mathrm{cal}}}{P_i^{\exp}} \right)^2 + \frac{0.84}{n_p} \sum_{i=1}^{n_P} \left(\frac{\rho_i^{\exp} - \rho_i^{\mathrm{cal}}}{\rho_i^{\exp}} \right)^2 \\
& + \frac{0.10}{n_w} \sum_{i=1}^{n_w} \left(\frac{w_i^{\exp} - w_i^{\mathrm{cal}}}{w_i^{\exp}} \right)^2 \\
& + \frac{0.04}{n_{C_p}} \sum_{i=1}^{n_{C_p}} \left(\frac{C_{p_i}^{\exp} - C_{p_i}^{\mathrm{cal}}}{C_{p_i}^{\exp} - C_{p_i}^{0}} \right)^2 + \frac{0.02}{n_{C_v}} \sum_{i=1}^{n_{C_v}} \left(\frac{C_{v_i}^{\exp} - C_{v_i}^{\mathrm{cal}}}{C_{v_i}^{\exp} - C_{v_i}^{0}} \right)^2 \qquad (6)
\end{aligned}
$$

Here n is the number of data points for each data type. The superscript 0 refers to the ideal gas state.

4.3. Incorporating the Results from Nonlinear Fitting in a Wide-Range Equation of State

P–ρ–T, w–ρ–T, and C_v–ρ–T data sets were calculated from the equation of state for the liquid region, developed with nonlinear regression techniques. The data set covered temperatures from 150 to 320 K, at pressures up to 60 MPa, and contained 195 data points for each property. The data were weighted using error propagation theory [19]. The uncertainties associated with these generated data were assumed to be the same as those given in Table II. These generated data as well as experimental data in other regions were incorporated in a wide-range equation of state using multiproperty, stepwise linear regression.

Table III summarizes the average absolute deviation (AAD) between the selected data used in the nonlinear regression and property values calculated from the original [2], preliminary, liquid, and interim wide-range equations of state. This table indicates that the deviations are almost identical for the original equation of state [2] and the preliminary equation of state. The equation for the liquid, developed using nonlinear regression techniques, exhibits lower speed-of-sound and isobaric heat capacity deviations without adversely affecting the representation of density. The isobaric heat capacity AAD for the interim wide-range equation of state is larger than that of the equation for the liquid. This is believed to be due to the inconsistency between the experimental data in the liquid region and saturation properties used in the correlation of the wide-range equation of state.

Table III. Percent Average Absolute Deviations Between Selected Data Used in the Nonlinear Regression and Property Values Calculated from Original [2], Preliminary, Liquid, and Interim Wide-Range Equations of State

Equation of state	ρ	w	C_p
Original [2]	0.000	0.774	1.704
Preliminary	0.001	0.770	1.694
Liquid	0.039	0.197	0.152
Interim wide-range	0.040	0.250	0.636

4.4. Accuracy Evaluation

Data sets from each interim equation were calculated at temperatures between 140 and 350 K. The procedures described above in Sections 4.1 through 4.3 were repeated until the temperature limit of the wide-range equations of state was lowered to the triple point. The coefficients for Eq. (3) are given in Table IV. Table V shows the average absolute deviation between the selected experimental data and the predicted values calculated from the original [2], interim, and the final wide-range equations of state. This table shows improvement in representing the saturated liquid isobaric heat capacity data by Neilson and White [18] through the iteration process. The final equation of state also represents the density data by Blanke and Weiss [9], Händel et al. [8], and Kohlen et al. [10] within ±0.05%. The data of Michels [11], Oguchi et al. [12], and Zander [13] show deviations larger than ±0.2% due to large deviations associated with a few data points located in the critical region. The final equation of state also represents the speed of sound data within ±0.3%.

Table IV. Coefficients and Exponents of the New Equation of State for HCFC-22

N_k	i_k	j_k	l_k	γ_k
$0.695645445236 \times 10^{-1}$	1	−1.000	0	0.0
$0.252275419999 \times 10^{2}$	1	1.750	0	0.0
$-0.202351148311 \times 10^{3}$	1	2.250	0	0.0
$0.350063090302 \times 10^{3}$	1	2.500	0	0.0
$-0.223134648863 \times 10^{3}$	1	2.750	0	0.0

Table IV. *(Continued)*

N_k	i_k	j_k	l_k	γ_k
$0.488345904592 \times 10^{2}$	1	3.000	0	0.0
$0.108874958556 \times 10^{-1}$	1	5.500	0	0.0
0.590315073614	2	1.500	0	0.0
−0.689043767432	2	1.750	0	0.0
0.284224445844	2	3.500	0	0.0
0.125436457897	3	1.000	0	0.0
$-0.113338666416 \times 10^{-1}$	3	4.500	0	0.0
$-0.631388959170 \times 10^{-1}$	4	1.500	0	0.0
$0.974021015232 \times 10^{-2}$	5	0.500	0	0.0
$-0.408406844722 \times 10^{-3}$	6	4.500	0	0.0
$0.741948773570 \times 10^{-3}$	7	1.000	0	0.0
$0.315912525922 \times 10^{-3}$	7	4.000	0	0.0
$0.876009723338 \times 10^{-5}$	7	5.000	0	0.0
$-0.110343340301 \times 10^{-3}$	8	−0.500	0	0.0
$-0.705323356879 \times 10^{-4}$	8	3.500	0	0.0
0.235850731510	2	5.000	2	−1.0
−0.192640494729	2	7.000	2	−1.0
$0.375218008557 \times 10^{-2}$	2	12.000	2	−1.0
$-0.448926036678 \times 10^{-4}$	2	15.000	2	−1.0
$0.198120520635 \times 10^{-1}$	3	3.500	3	−1.0
$-0.356958425255 \times 10^{-1}$	4	3.500	2	−1.0
$0.319594161562 \times 10^{-1}$	4	8.000	2	−1.0
$0.260284291078 \times 10^{-5}$	4	15.000	2	−1.0
$-0.897629021967 \times 10^{-2}$	4	25.000	4	−1.0
$0.345482791645 \times 10^{-1}$	6	3.000	2	−1.0
$-0.411831711251 \times 10^{-2}$	6	9.000	2	−1.0
$0.567428536529 \times 10^{-2}$	6	19.000	4	−1.0
$-0.563368989908 \times 10^{-2}$	8	2.000	2	−1.0
$0.191384919423 \times 10^{-2}$	8	7.000	2	−1.0
$-0.178930036389 \times 10^{-2}$	8	13.000	4	−1.0

Table V. Percent Average Absolute Deviations Between Selected Data and Property Values Calculated from the Original [2], Interim, and Final Wide-Range Equations of State

		Equation of state		
Experimental data set	No. of data	Original [2]	Interim	Final
P–ρ–T data				
Blanke and Weiss [9]	178	0.062	0.176	0.048
Händel et al. [8]	55	0.049	0.063	0.013
Kohlen et al. [10]	90	0.055	0.055	0.089
Michels [11]	182	0.351	0.327	0.286
Oguchi et al. [12]	100	0.249	0.273	0.266
Zander [13]	272	0.336	0.345	0.340
Total	877	0.227	0.251	0.215

Table V. *(Continued)*

Experimental data set	No. of data	Equation of state Original [2]	Interim	Final
w–P–T data				
Blanke and Weiss [9]	51	0.247	0.220	0.231
Meyer [20]	9	0.441	0.330	0.241
Niepmann et al. [14]	110	0.261	0.274	0.243
Total	170	0.267	0.261	0.239
C_p–*P*–*T* data				
Bier et al. [18]	16	0.316	0.562	0.398
Ernst and Busser [17]	37	0.310	0.382	0.219
Neilson and White [15]	12	21.252	11.785	0.341
Tanisha et al. [16]	39	0.249	0.239	0.232
Total	104	2.704	1.672	0.265

5. CONCLUSIONS

A new wide-range equation of state for HCFC-22 was developed using nonlinear regression to improve the representation of the derived property data in the liquid region. The new formulation covers temperatures from 115.73 to 550 K. The high-pressure limit is 60 MPa for temperatures above 200 K and 10 MPa for temperatures below 200 K. The uncertainties of predicted properties are ±0.1% for density, ±0.3% for speed of sound, and ±1.0% for heat capacity.

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