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A Thermodynamic Property Formulation for Air. I. Single-Phase Equation of State from 60 to 873 K at Pressures to 70 MPa[1]

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A revised interim formulation for the thermodynamic properties of air has been developed for calculating properties of the vapor and estimating properties for the liquid at temperatures as low as 60 K. The formulation incorporates separate equations for the calculation of bubble-point and dew-point pressures and densities and for the ideal-gas heat capacity. A new fundamental equation of state is given for vapor and liquid states of air based upon available experimental data and predicted values of isochoric heat capacity for the liquid using corresponding states methods. Procedures for predicting C_v are discussed. The fundamental equation for air is explicit in nondimensional Helmholtz energy. The terms of the fundamental equation were selected from a larger set of 75 proposed terms using a least-squares fitting procedure. Representative graphical comparisons of calculated property values to experimental measurements are given. The estimated accuracy of calculated densities is generally ±0.2% except near the dew and bubble lines. Calculated heat capacities for the liquid must be considered only as estimates until substantiated by experimental measurements.

KEY WORDS: air; density; equation of state; fundamental equation; heat capacity; thermodynamic properties; velocity of sound.

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1. INTRODUCTION

A revised interim thermodynamic property formulation for air has been developed for states from 60 to 873 K at pressures to 70 MPa. This formulation supersedes that given in Ref. 1 and allows the calculation of estimated low-temperature liquid properties down to 60 K. The interim status of this formulation recognizes the need for further measurement of the thermodynamic properties of air and similar N_2–Ar-O_2 mixtures. The formulation incorporates new values for the high-pressure bubble-point and dew-point properties of air superseding those of Rainwater and Jacobsen [2]. Details of the development of the bubble and dew line property calculations are given in Ref. 3. A new fundamental equation of state is given for vapor and liquid states of air based upon available experimental data and predicted values of isochoric heat capicty (C_v). The liquid properties from this formulation are based on limited pressure–density–temperature (P–ρ–T) data, including the data of Vasserman et al. [4], and on isochoric heat capacities predicted using the method of corresponding states.

The estimated accuracy of calculated density values for the vapor is $\pm 0.2\%$ except near the dew line, where the accuracy is estimated as $\pm 0.5\%$. Calculated liquid densities are believed to be accurate to within $\pm 0.2\%$ except near the bubble line where the error may be $\pm 2\%$. The estimated accuracy is $\pm 2\%$ for calculated values of heat capacity in the liquid, although these estimates cannot be substantiated by comparisons to experimental measurements. The accuracy of the representation of the critical region by the model is unknown. The use of this formulation for states near the critical point of air is not recommended because analytic formulations generally fail to represent critical-state anomalies.

2. AIR COMPOSITION

Atmospheric air is a mixture of fluids including nitrogen, oxygen, argon, carbon dioxide, water vapor, and other trace elements. We have elected to treat only dry air in this work and to neglect carbon dioxide and the trace elements as possible constituents. The composition of air for the development of the wide-range property formulation reported here is taken from Jones [5] which is essentially consistent with that of the U.S. Standard Atmosphere [6]. Other compositions are given in Refs. 7 and 8. Based upon the recommendations for the composition of air of Olien [9], and assuming that carbon dioxide is not present, this composition, given in mole fractions, is 0.7812 nitrogen, 0.2096 oxygen, and 0.0092 argon.

3. THE FUNDAMENTAL EQUATION FOR AIR

With some exceptions, the fundamental equation for air represents selected experimental and calculated property values to within the estimated uncertainties of these values. Table I gives a summary of experimental P–ρ–T data for air. The low-density data of Stewart et al. [18] were calculated from a truncated virial equation for air. Details are given in Ref. 18. The data selected for developing the fundamental equation here are identified in Table I. The loci of the experimental P–ρ–T data presented in Table I are illustrated in Fig. 1. Values of C_v for liquid states below the critical temperature predicted using the extended corresponding-states approach described by Eaton et al. [19] were included in the data set used to develop the fundamental equation. For the extended corresponding-states prediction of C_v values, air was treated as a binary mixture of 78.85% nitrogen and 21.15% oxygen. This composition was obtained by normalizing the mole fractions given in Section 2, neglecting the presence of argon. The accurate oxygen formulation of Schmidt and Wagner [20] was used as the reference fluid. The loci of predicted C_v data are illustrated in Fig. 2. The velocity of sound data of Van Itterbeek and de Rop [21] illustrated in Fig. 2 were not used in developing the fundamental equation, but comparisons to these measurements are included in Section 4.

Table I. Summary of Selected P–ρ–T Data for Air

		Range of Values			
Reference	Year	Pressure (MPa)	Density ($\mathrm{mol \cdot dm^{-3}}$)	Temperature (K)	No. of points
Blanke [10][a]	1977	0.007–5	0.02–33	60–169	142
Holborn and Schultze [11]	1915	2–10	0.6–4.5	273–473	42
Kozlov [12][a]	1968	1–72	0.2–17	298–873	340
Michels et al. [13][a]	1954	0.6–102	0.3–25	118–248	187
Michels et al. [14][a]	1954	0.7–228	0.3–29	273–348	157
Penning [15]	1923	2.5–6.2	1.2–4.5	128–293	63
Rogovaya and Kagner [16]	1960	1.9–11	1.4–11.4	173.15–273.15	23
Romberg [17][a]	1971	0.022–2	0.03–2.7	84–122	124
Stewart et al. [18][a]	1985	0.01–4	0.001–3.89	74–873	356
Vasserman et al. [4][a]	1976	2.6–60	22.8–31.4	77–199	109

[a] Data selected for developing the fundamental equation.

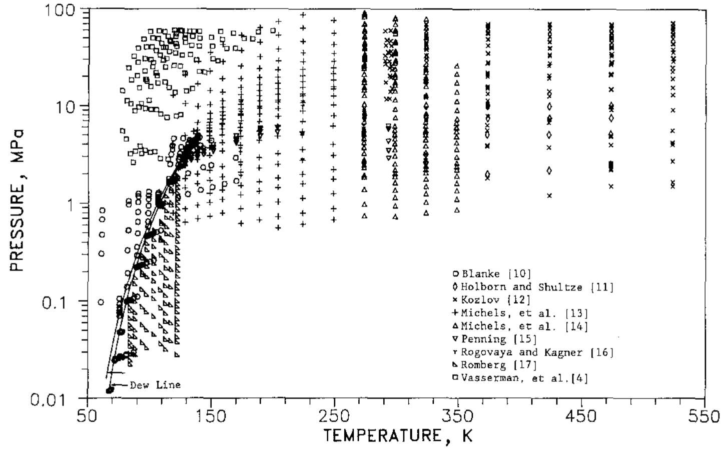

Fig. 1. Experimental P–ρ–T data points for air.

The functional form used for the fundamental equation for air is explicit in nondimensional Helmholtz energy

$$\alpha(\delta, \tau) = [A(\rho, T)]/RT = \alpha^0 + \bar{\alpha}(\delta, \tau) \tag{1}$$

where α^0 is the reduced ideal-gas contribution to the Helmholtz energy, $\bar{\alpha}$ is the reduced real-fluid contribution to the Helmholtz energy, $\delta = \rho/\rho_j$, $\tau = T_j/T$, ρ_j is the density at the maxcondentherm from Ref. 3 (10.45

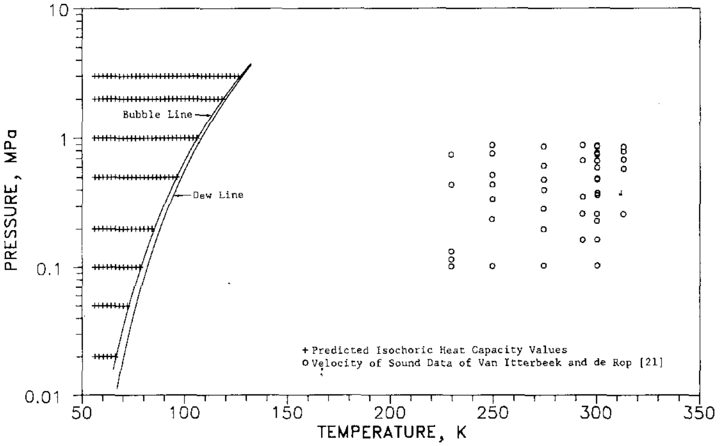

Fig. 2. Predicted isochoric heat capacity values and experimental velocity of sound data points for air.

mol·dm^{-3}), T_j is the temperature at the maxcondentherm from Ref. 3 (132.6639K), and R is the gas constant, 0.00831451 (MPa·dm^3·mol^{-1}·K^{-1}).

The α^0 for air is determined by

$$\alpha^0 = \sum_{i=1}^{3} x_i \left[\frac{A_i^0(\rho, T)}{RT} + \ln(x_i) \right] \tag{2}$$

where A_i^0 is the ideal-gas Helmholtz Energy of pure component i, and x_i is the mole fraction of component i in air given in Section 2. Functions for the A_i^0/RT of nitrogen, argon, and oxygen are given in Refs. 22, 23, and 24.

The real-fluid contribution to dimensionless Helmholtz energy is given by

$$\bar{\alpha}(\delta, \tau) = \sum_{k=1}^{30} N_k \delta^i \tau^j \exp(-\gamma \delta^l) \tag{3}$$

where the N_k are the coefficients of the fundamental equation, and γ is a coefficient which has a value of 0 for terms with $l = 0$ and a value of 1 for terms with l greater than zero. Values of N_k, i, j, and l are given in Table II. The functional form of the fundamental equation includes terms suggested by Schmidt and Wagner [20]. The coefficients of the equation developed in this work were selected from an initial group of 75 proposed terms by a least-squares selection algorithm originally developed by Wagner [25] and adapted for equations of state by de Reuck and Armstrong [26].

4. COMPARISONS OF THERMODYNAMIC PROPERTIES CALCULATED FROM THE FUNDAMENTAL EQUATION TO EXPERIMENTAL DATA

Thermodynamic properties of air may be calculated from the fundamental equation using the appropriate derivatives of the reduced Helmholtz energy. Detailed comparisons of calculated property values to available experimental measurements were made to estimate the accuracy of this thermodynamic property formulation. A summary of these comparisons is presented in Table III.

The estimated uncertainty of densities calculated from the fundamental equation is ±0.2% for subcritical liquid states down to 60 K. Comparisons for supercritical and subcritical vapor states down to 80 K indicate an estimated uncertainty in calculated densities of ±0.1%. For vapor states below 80 K, the uncertainty of density values from the fundamental equation is between ±0.3 and ±0.5%.

The fundamental equation represents the C_v values obtained from the extended corresponding-states prediction to within ±0.2%. Because the predicted C_v values from extended corresponding states have an estimated uncertainty of ±2%, C_v values calculated from the fundamental equation also have an uncertainty of ±2%.

Values of calculated velocity of sound deviate less than ±0.2% from the measurements of Van Itterbeek and de Rop [21] for the vapor states with the exception of the isotherm at 300 K. An unexplained systematic deviation of about 0.4% is evident on the 300 K isotherm.

The ability of this formulation to model the thermodynamic surface of air in the critical region is unknown because the critical region for air is not

Table II. Coefficients and Exponents for the Fundamental Equation (3) for Air

k	N_k	i	j	l
1	0.1071142974	1	0.00	0
2	1.278538204	1	0.50	0
3	−7.750912747	1	1.25	0
4	8.504674647	1	1.50	0
5	−3.089980461	1	1.75	0
6	0.01878338005	2	−0.50	0
7	0.1468295591	2	1.50	0
8	$0.7073042217 \times 10^{-4}$	2	6.00	0
9	−0.07623976863	3	0.00	0
10	0.1656970669	3	0.25	0
11	−0.1150366042	3	1.00	0
12	$-0.2080560676 \times 10^{-2}$	3	3.00	0
13	$0.2720930418 \times 10^{-2}$	4	0.25	0
14	$-0.7173878616 \times 10^{-3}$	6	0.00	0
15	$0.1500827773 \times 10^{-2}$	6	0.50	0
16	$0.3183053255 \times 10^{-3}$	6	2.50	0
17	$-0.6699843082 \times 10^{-6}$	7	5.00	0
18	$-0.2282008536 \times 10^{-4}$	8	2.00	0
19	−0.1139209864	1	5.00	2
20	0.03721482836	1	6.00	2
21	−0.04704866287	3	7.00	2
22	$-0.6022871245 \times 10^{-2}$	4	1.50	2
23	0.01498130985	5	6.00	2
24	$-0.4533718156 \times 10^{-3}$	6	8.50	2
25	$-0.1416096755 \times 10^{-2}$	8	1.00	2
26	$0.2910235410 \times 10^{-3}$	10	5.50	2
27	$0.7040990750 \times 10^{-2}$	1	1.50	3
28	$-0.1827037232 \times 10^{-2}$	4	2.00	4
29	$0.9901699323 \times 10^{-2}$	4	11.00	4
30	$-0.7856319485 \times 10^{-2}$	4	23.00	4

well defined by experiment, and the behavior of the mixture in the critical region is not properly represented by this model. Consequently, the use of this formulation for calculating properties in the density range from 8.25 to 13.75 $\mathrm{mol \cdot dm^{-3}}$ with temperatures from 128 to 136 K is not recommended.

Table III. Summary of Comparisons of Calculated Properties of Air to Experimental Data

Reference	RMS Percentage Deviation[a]		No. of Points
	Pressure	Density	
P–ρ–T data above the critical temperature			
Blanke [10]	0.105595	0.484578	22
Holborn and Schultze [11]	0.033865	0.033146	42
Kozlov [12]	0.042588	0.035327	336
Michels et al. [14]	0.022497	0.012712	157
Michels et al. [13]	0.046140	0.098445	172
Penning [15]	0.048931	0.069079	53
Rogovaya and Kagner [16]	0.148495	0.172190	23
Vasserman et al. [4]	0.383459	0.075340	22
Vapor P–ρ–T data below the critical temperature			
Blanke [10]	0.189342	0.206569	45
Michels et al. [13]	0.029310	0.90521	17
Penning [15]	0.057970	0.116839	10
Romberg [17]	0.028402	0.033068	124
Liquid P–ρ–T data below the critical temperature			
Blanke [10]		0.043605	49
Michels et al. [13]		0.230804	8
Vasserman et al. [4]		0.066310	87
Isochoric heat capacity data			
	C_v		
Predicted values (this work)	0.046666		139
Velocity of sound data			
	Vel. of sound		
Van Itterbeek and de Rop [21]			
Wide range	0.127881		28
300K only	0.339514		15

[a] RMS Percentage deviation of property $X = \sum_{i=1}^{N} [\mathrm{Dev}(X_i)]^2/N$, where $\mathrm{Dev}(X_i) = 100[X_i^{(\mathrm{data})} - X_i^{(\mathrm{calc})}]/X_i^{(\mathrm{data})}$.

Table IV. Summary of Thermodynamic Property Correlations for Air

Reference	Year	Temperature range (K)	High-pressure limit (MPa)
Hilsenrath et al. [27]	1955	50–3000	10
Michels et al. [28]	1955	102–348	122
Din [29]	1956	90–450	122
Baehr and Schwier [30]	1961	60–1250	450
Vasserman and Rabinovich [31][a]	1968	75–160	50
Vasserman et al. [32][b]	1971	75–1300	100
Sychev et al. [33][c]	1978	70–1500	100
Jacobsen et al. [1]	1987	85–873	70

[a] Liquid states.

[b] Vapor states.

[c] English translation published in 1987.

5. PRIOR CORRELATIONS ON THE THERMODYNAMIC PROPERTIES OF AIR

Several wide-range property correlations for air have been published during the past 30 years. Table IV is a summary of prior correlations. Although many of these thermodynamic property tables are still being used today, none has the ability to represent compressed liquid properties at low temperatures. The treatment of air as a pseudopure fluid introduces some deficiencies in the formulation, particularly for properties on or near the dew and bubble lines, but the results are sufficiently accurate for most engineering needs. The current formulation is believed to be an improvement over prior work because of the inclusion of both liquid P–ρ–T data and predicted liquid C_v data in the data set used for determining the equation of state.

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