

Thermodynamic Properties of Air from 60 to 2000 K at Pressures up to 2000 MPa¹

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A thermodynamic property formulation for standard dry air based upon experimental P - ρ - T , heat capacity, and speed of sound data and predicted values, which extends the range of prior formulations to higher pressures and temperatures, is presented. This formulation is valid for temperatures from the solidification temperature at the bubble point curve (59.75 K) to 2000 K at pressures up to 2000 MPa. In the absence of experimental air data above 873 K and 70 MPa, air properties were predicted from nitrogen data. These values were included in the fit to extend the range of the fundamental equation. Experimental shock tube measurements ensure reasonable extrapolated properties up to temperatures and pressures of 5000 K and 28 GPa. In the range from the solidification point to 873 K at pressures to 70 MPa, the estimated uncertainty of density values calculated with the fundamental equation for the vapor is $\pm 0.1\%$. The uncertainty in calculated liquid densities is $\pm 0.2\%$. The estimated uncertainty of calculated heat capacities is $\pm 1\%$ and that for calculated speed of sound values is $\pm 0.2\%$. At temperatures above 873 K and 70 MPa, the estimated uncertainty of calculated density values is $\pm 0.5\%$, increasing to $\pm 1\%$ at 2000 K and 2000 MPa.

KEY WORDS: air; equation of state; fundamental equation; high pressure; high temperature; thermodynamic properties.

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1. INTRODUCTION

In certain applications using air as a working fluid, system modeling requirements include the need for thermophysical properties of air at pressures up to 2000 MPa and at temperatures up to 2000 K. A new equation of state, which supersedes the previous model of Jacobsen et al. [1], for the thermodynamic properties of air has been developed and extends the equation to higher temperatures and pressures. It is based upon the work of Panasiti [2].

Only dry air containing no carbon dioxide or trace elements was studied. The composition of air used in this work is that from the previous work of Jacobsen et al. [1] given in mole fractions as 0.7812 nitrogen, 0.0092 argon and 0.2096 oxygen. At high temperatures, air and its constituents dissociate, and the composition changes to include various atomic and ionic species and new compounds including oxides of nitrogen. An analysis by Panasiti [2], based on the Peng–Robinson [3] equation of state, indicated that dissociation effects are small enough that they could be neglected in the development of the new property formulation for air.

2. CALCULATION OF AIR PROPERTIES FROM NITROGEN DATA

Experimental P – ρ – T measurements for nitrogen extend to 1800 K and 2220 MPa. Air properties were calculated from high-pressure and high-temperature nitrogen data using the following relationships for temperature and density:

$$T_{\text{air}} = \frac{T_{\text{N}_2}}{T_{c_{\text{N}_2}}} T_{c_{\text{air}}} \quad \text{and} \quad \rho_{\text{air}} = \frac{\rho_{\text{N}_2}}{\rho_{c_{\text{N}_2}}} \rho_{c_{\text{air}}} \quad (1, 2)$$

where the subscript c represents the critical properties for nitrogen and pseudo-critical properties for air. The pressure was calculated by assuming that

$$P_{\text{air}}(\rho_{\text{air}}, T_{\text{air}}) = \frac{\rho_{c_{\text{air}}} T_{c_{\text{air}}}}{\rho_{c_{\text{N}_2}} T_{c_{\text{N}_2}}} P_{\text{N}_2}(\rho_{\text{N}_2}, T_{\text{N}_2}) \quad (3)$$

To optimize the correspondence between nitrogen data and the air equation of state of Jacobsen et al. [1], the pseudo-critical temperature $T_{c_{\text{air}}}$ and density $\rho_{c_{\text{air}}}$ for air were modified using nonlinear least-squares fits to selected nitrogen data of Jaeschke and Humphreys [4] and Straty and Diller [5] in the range of 140 to 353 K up to pressures of 34.8 MPa. This

fitting procedure minimized deviations between air properties estimated from nitrogen data and values from the equation for air by Jacobsen et al. [1]. The average absolute deviation was 0.01% for the nitrogen data of Jaeschke and Humphreys [4] and was 0.1% for the data of Straty and Diller [5] from values calculated using the equation of state for nitrogen. The resulting reducing parameters are $T_{\text{c,air}} = 132.69$ K and $\rho_{\text{c,air}} = 11.71$ mol · dm⁻³. The average absolute deviations for the transformed air data at points defined by these two data sets from values calculated using the equation of state for air were 0.06% and 0.3%, respectively. The estimated uncertainty of calculated air properties is within $\pm 1\%$ in density at the highest temperatures and pressures of 2000 K and 2000 MPa.

3. DEVELOPMENT OF A NEW THERMODYNAMIC PROPERTY FORMULATION FOR AIR

3.1. Fixed Points for Air

The maxcondentherm, maxcondenbar, and critical point for air used in this work were reported by Jacobsen et al. [6]. These values were determined using a Leung–Griffiths model modified for the ternary system N₂–Ar–O₂. The values of the properties at the maxcondentherm were used as reducing parameters for the fundamental equation presented here. The fixed point properties for air used in this work are given in Table I and illustrated in Fig. 1. This figure also shows calculated densities from the equation of state given here and from the equation of state presented by Jacobsen et al. [1] at specified temperatures and the bubble- or dew-point pressures. The equation presented here is a more accurate representation of values from the Leung–Griffiths model [6] than the previous equation [1]. The temperatures are given on the International Temperature Scale of 1990 (ITS-90). The molar mass of air used in this work is 28.9585 g · mol⁻¹, and the universal gas constant is 8.31451 J · mol⁻¹ · K⁻¹.

Table I. Fixed Point Properties for Air

	Pressure (MPa)	Temperature (K)	Density (mol · dm ⁻³)
Maxcondentherm ^a	3.78502	132.6312	10.4477
Maxcondenbar	3.7891	132.6035	11.0948
Critical point	3.7860	132.5306	11.8308

^a Values used for the reducing parameters in the equation of state.

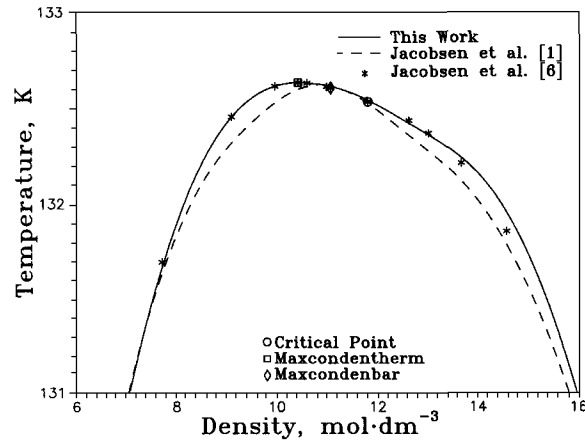


Fig. 1. Dew- and bubble-point curves for air in the critical region.

3.2. Ancillary Equations for Air

Ancillary equations representing the bubble- and dew-point pressures and densities are described in detail by Penoncello et al. [7]. The equations and coefficients from Ref. 7 were used in calculations to define the liquid-vapor boundaries as described in Section 3.4.

3.3. Freezing Liquid Line for Air

Lemmon [8] reported a freezing liquid line equation for air which was used in the prior formulation of Jacobsen et al. [1]. This equation uses the solidification temperature, $T_s = 59.75$ K, of air at the bubble-point curve given by Blanke [9]. The solidification pressure P_s at this triple point was calculated from the bubble-point pressure curve as 0.0062545 MPa. The reduced pressure along the freezing liquid line is given as a function of the reduced temperature,

$$\ln\left(\frac{P}{P_s}\right) = N_1\theta^{1/16} + N_2\theta^{1/8} + N_3\theta^{3/16} + N_4\theta^{1/4} + N_5\theta^{5/16} \quad (4)$$

where $\theta = (T/T_s - 1)$. The coefficients for the freezing liquid pressure equation are given in Table II.

Table II. Coefficients for the Freezing Liquid Pressure Eq. (4) for Air

k	N_k
1	$-0.205\,394\,8 \times 10^2$
2	$0.444\,658\,7 \times 10^2$
3	$0.357\,496\,0 \times 10^2$
4	$-0.870\,591\,1 \times 10^2$
5	$0.385\,677\,1 \times 10^2$

3.4. The Fundamental Equation for Air

The fundamental equation was developed using experimental pressure–density–temperature (P – ρ – T), isochoric heat-capacity, and speed-of-sound data and the calculated air properties at high temperatures and pressures described in Section 2. P – ρ – T values on the dew and bubble point curves calculated using the ancillary equations from Penoncello et al. [7] were used to define the vapor-liquid equilibrium boundaries. To increase the range of the equation beyond 2000 K and 2000 MPa, a single datum published by Nellis et al. [10], determined using a shock tube apparatus, was included in the fitting process. The fundamental equation for air used in this work is explicit in the nondimensional Helmholtz energy,

$$\alpha(\delta, \tau) = \frac{A(\rho, T)}{RT} = \alpha^\circ(\delta, \tau) + \alpha^r(\delta, \tau) \quad (5)$$

where α° is the ideal-gas contribution to the nondimensional Helmholtz energy, α^r is the residual contribution to the nondimensional Helmholtz energy, $\delta = \rho/\rho_j$ is the reduced density, $\tau = T_j/T$ is the reciprocal reduced temperature, ρ_j is the density at the maxcondentherm, T_j is the temperature at the maxcondentherm, and R is the ideal gas constant. The ideal gas contribution to the nondimensional Helmholtz energy for air is given by

$$\begin{aligned} \alpha^\circ(\delta, \tau) = & -1 + \ln \frac{\delta \tau_o}{\delta_o \tau} - \frac{\tau}{R} \int_{\tau_o}^{\tau} \frac{C_p^\circ}{\tau^2} d\tau + \frac{1}{R} \int_{\tau_o}^{\tau} \frac{C_p^\circ}{\tau} d\tau \\ & + \sum_{i=1}^3 x_i \left[\frac{H_{o,i}^\circ \tau}{RT_j} - \frac{S_{o,i}^\circ}{R} + \ln x_i \right] \end{aligned} \quad (6)$$

Table III. Values of H_o° and S_o° for Nitrogen, Argon, and Oxygen [11]

	Nitrogen	Argon	Oxygen
H_o° (J · mol ⁻¹)	8670	6197	8680
S_o° (J · mol ⁻¹ · K ⁻¹)	191.5	154.737	205.043

where x_i is the mole fraction of component i in air, $\tau_o = T_j/T_o$, $\delta_o = \rho_o/\rho_j$ is the reduced ideal gas density at P_o and T_o , T_o is the reference temperature (298.15 K), P_o is the reference pressure (0.101325 MPa), $H_{o,i}^\circ$ is the reference enthalpy at T_o , and $S_{o,i}^\circ$ is the reference entropy at T_o and P_o . Values of H_o° and S_o° for nitrogen, argon, and oxygen taken from Cox et al. [11] are given in Table III.

The ideal gas heat capacity C_p° for air is calculated by combining the ideal gas heat capacity equation for nitrogen from Jacobsen et al. [12], an equation for oxygen, modified from that of the original work of Schmidt and Wagner [13] by the elimination of one term, and the expression for a monatomic gas, $C_p^\circ = 5/2R$, for argon. The ideal gas heat capacity for air is then

$$\frac{C_p^\circ}{R} = \sum_{i=1}^7 C_i T^{i-4} + \frac{C_8}{T^{1.5}} + \frac{C_9 u^2 e^u}{(e^u - 1)^2} + \frac{C_{10} v^2 e^v}{(e^v - 1)^2} \quad (7)$$

Table IV. Coefficients of the Ideal Gas Isobaric Heat Capacity Eq. (7) for Air

k	C_k
1	-0.6539268×10^3
2	0.2961897×10^2
3	-0.4700776
4	0.3494156×10^1
5	$-0.6835154 \times 10^{-5}$
6	0.1513614×10^{-7}
7	$-0.2002765 \times 10^{-11}$
8	0.2238067
9	0.2122368
10	0.7872444
11	0.224245×10^4
12	0.33534061×10^4

where $u = C_{11}/T$ and $v = C_{12}/T$. The coefficients for Eq. (7) are given in Table IV. The resulting expression for α° is obtained by combining Eqs. (6) and (7),

$$\alpha^\circ = \ln \delta + \sum_{i=1}^7 M_i \tau^{i-4} + M_8 \tau^{1.5} + M_9 \ln \tau + M_{10} \tau \ln \tau \\ + M_{11} \ln[1 - \exp(-M_{13} \tau)] + M_{12} \ln[1 - \exp(-M_{14} \tau)] \quad (8)$$

The coefficients for Eq. (8) are given in Table V.

The real fluid contribution to the nondimensional Helmholtz energy is given by

$$\alpha^r(\delta, \tau) = \sum_{k=1}^{33} N_k \delta^k \tau^k \exp(-\gamma \delta^k) \quad (9)$$

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 0. The coefficients for Eq. (9) are given in Table VI. All thermodynamic properties can be calculated from the Helmholtz energy using differentiation with respect to density or temperature as described by Lemmon et al. [14].

Table V. Coefficients of the Ideal Gas Helmholtz Energy Eq. (8) for Air

k	M_k
1	$0.389\,390\,9 \times 10^{-6}$
2	$-0.443\,767\,3 \times 10^{-4}$
3	$0.453\,277\,3 \times 10^{-3}$
4	$-0.138\,238\,9 \times 10^2$
5	$-0.120\,444\,7 \times 10^{-1}$
6	$-0.841\,876\,8 \times 10^{-3}$
7	$0.467\,133\,3 \times 10^{-4}$
8	$-0.195\,363\,4 \times 10^{-3}$
9	$0.249\,415\,6 \times 10^1$
10	$0.354\,424\,6 \times 10^{-2}$
11	0.212 236 8
12	0.787 244 4
13	$0.169\,074\,1 \times 10^2$
14	$0.252\,836\,9 \times 10^2$

Table VI. Coefficients and Exponents for the Fundamental Eq. (9) for Air

k	N_k	i_k	j_k	l_k
1	$0.653047013811 \times 10^{-1}$	1	0	0
2	0.678835009195	1	0.25	0
3	$-0.143490786106 \times 10^1$	1	1	0
4	$-0.321903633516 \times 10^{-2}$	1	3.5	0
5	$0.583911230624 \times 10^{-1}$	2	0	0
6	$0.239601980951 \times 10^{-1}$	4	0.5	0
7	$-0.584000786794 \times 10^{-1}$	3	0	0
8	0.137011320694	3	0.25	0
9	$0.219932875035 \times 10^{-3}$	3	3.5	0
10	$0.837104476841 \times 10^{-2}$	4	0	0
11	$-0.306746271489 \times 10^{-1}$	4	0.25	0
12	$0.338386156676 \times 10^{-4}$	6	0.5	0
13	$0.164630578408 \times 10^{-5}$	8	2	0
14	-0.176893815222	1	1.5	1
15	-0.353933053336	3	1	1
16	$-0.566621330528 \times 10^{-1}$	5	1	1
17	-0.190100444223	1	3	2
18	$-0.215976092083 \times 10^{-2}$	1	8	2
19	$-0.308948799371 \times 10^{-2}$	3	9	2
20	$0.293942842065 \times 10^{-3}$	11	3	2
21	$0.293832797468 \times 10^{-1}$	1	3	3
22	$-0.321576125494 \times 10^{-1}$	3	13	3
23	$0.554138225907 \times 10^{-2}$	4	22	4
24	$-0.542472707547 \times 10^{-2}$	5	23	4
25	$0.205042936393 \times 10^{-2}$	2	11	5
26	$-0.219851045253 \times 10^{-1}$	6	1	1
27	$0.128752208849 \times 10^{-1}$	3	0.5	2
28	$-0.219001412602 \times 10^{-1}$	3	5.5	2
29	$0.390910141344 \times 10^{-5}$	12	6	2
30	$-0.574114394530 \times 10^{-2}$	3	2	3
31	$0.182974806200 \times 10^{-1}$	4	13	3
32	$-0.142919356764 \times 10^{-2}$	9	11	3
33	$-0.225716528368 \times 10^{-2}$	3	11	5

4. COMPARISONS AND ASSESSMENT OF ACCURACY

Comparisons of calculated property values to available experimental measurements were made to assess the accuracy of the formulation. Detailed graphical and tabular comparisons to all available data are given by Panasiti [2].

Plots of constant property lines in various thermodynamic coordinates are useful in assessing the behavior of the fundamental equation. The fundamental equation developed here was used to produce plots of C_v and W vs. T along isobars as shown in Figs. 2 and 3. Table VII shows comparisons of properties calculated using the fundamental Eq. (5) to groups of experimental data. These comparisons report the absolute average deviations (AAD), the biases, the standard deviations (Std. Dev.), and the root mean square (RMS) deviations. The deviation of a property X is defined as $\% \Delta X = 100[(X_{\text{data}} - X_{\text{eos}})/X_{\text{data}}]$. Twenty-one data points with deviations greater than 10% were excluded in the calculated statistics. These outliers generally deviated from other reliable data in the same region.

In the range of available experimental data, the estimated uncertainty of density values calculated with Eq. (5) for the vapor is generally $\pm 0.1\%$. At temperatures above 873 K or pressures above 70 MPa, the estimated uncertainty of calculated density values is $\pm 0.5\%$, increasing to $\pm 1\%$ at 2000 K and 2000 MPa. The estimated uncertainty in calculated liquid

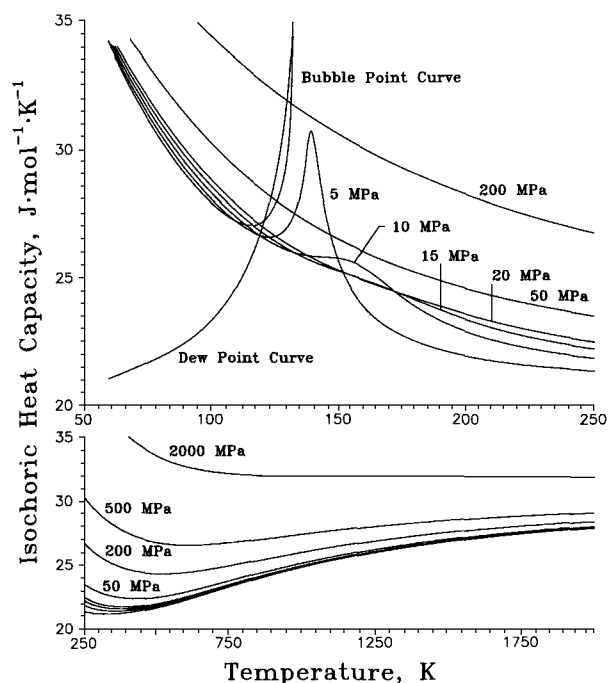


Fig. 2. Isochoric heat capacity for air, along isobars and along the dew- and bubble-point boundaries.

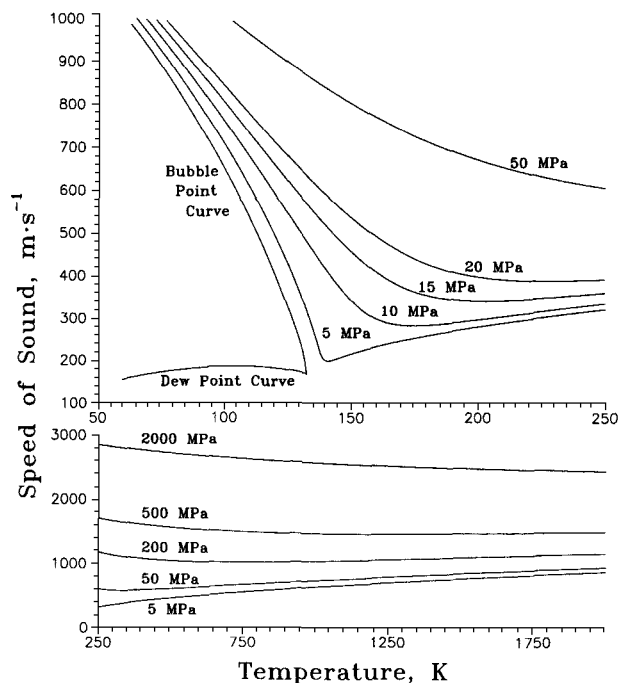


Fig. 3. Speed of sound for air, along isobars, and along the dew- and bubble-point boundaries.

densities is within $\pm 0.2\%$, for calculated values of heat capacities it is $\pm 1\%$, and for calculated values of the speed of sound it is $\pm 0.2\%$. Without experimental data, the uncertainty of extrapolated properties cannot be verified.

The accuracy of this formulation in the critical region is also uncertain partly because the critical region for air has not been measured extensively. This formulation should be used with caution for calculating properties at densities from 9.25 to $12.75 \text{ mol} \cdot \text{dm}^{-3}$ at temperatures from 130 to 134 K .

The recommended procedure for the calculation of bubble or dew properties at a given temperature is to use an ancillary function to calculate pressure and then use T and P as independent variables in the fundamental equation to calculate the remaining properties. With the exception of the critical region, the fundamental equation agrees within $\pm 0.3\%$ in density with P - ρ - T values on the bubble and dew point curves calculated using ancillary functions. As shown in Fig. 1, the fundamental equation of this work represents the predicted data of Jacobsen et al. [6] more accurately than the previous equation of state for air published by Jacobsen et al. [1].

Table VII. Statistical Analysis of Comparisons

Reference	No. of points	AAD (%)	Bias (%)	SD (%)	RMS (%)	Max. dev. (%)
<i>P</i> - ρ - <i>T</i> data						
Amagat [15]	78	0.224	-0.179	0.215	0.279	-0.696
Blanke [16]	130	0.351	-0.224	0.747	0.777	-4.595
Holborn and Schultze [17]	42	0.021	0.008	0.025	0.026	0.058
Howley et al. [18]	285	0.042	0.025	0.049	0.055	0.223
Kozlov [19]	348	0.063	-0.023	0.402	0.402	-7.099
Michels et al. [20]	199	0.167	-0.132	0.576	0.590	-5.644
Michels et al. [21]	157	0.028	0.025	0.023	0.034	0.067
Penning [22]	62	0.087	-0.011	0.101	0.101	-0.282
Rogovaya and Kaganer [23]	23	0.090	-0.057	0.190	0.189	-0.585
Romberg [24]	112	0.019	0.013	0.019	0.023	0.067
Vasserman et al. [25]	109	0.071	-0.022	0.086	0.089	-0.257
Overall	1545	0.099	-0.044	0.370	0.373	-7.099
Isochoric heat capacity						
Magee [26]	231	0.349	0.039	0.480	0.480	-2.144
Isobaric heat capacity						
Bridgeman [27]	51	0.922	-0.484	1.133	1.222	-3.658
Nesselmann [28]	19	1.816	-0.714	2.606	2.635	8.007
Pofelr et al. [29]	36	1.454	1.175	2.040	2.329	6.325
Overall	106	1.263	0.038	1.960	1.951	8.007
Speed of sound						
Goodwin [30]	13	0.009	0.008	0.011	0.014	0.040
van Itterbeek and de Rop [31]	44	0.214	0.144	0.308	0.336	1.769
Younglove and Frederick [32]	169	0.237	-0.068	0.497	0.500	-4.226
Overall	226	0.219	-0.023	0.458	0.457	-4.226

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