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Prediction of Thermodynamic Properties of Liquid Air

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Abstract In this work, a simple equation of state (EoS) has been used to predict some thermodynamic properties of air as a pseudo-pure fluid; as a ternary mixture of nitrogen, oxygen, and argon; and as a binary mixture of nitrogen and oxygen at different temperatures and pressures. A comparison with literature tabulated values has been made. The agreement of calculated densities with corresponding tabulated values is good for which the average absolute deviations are better than 0.06% if we assume air as a pseudo-pure fluid, and 0.9% and 1.2% if we consider air as a ternary mixture and as a binary mixture, respectively. To show the ability of this equation of state to predict density, the calculated densities of air have been compared with those computed by other methods.

Keywords Air · Density · GMA equation of state · Heat capacity

1 Introduction

The development of equations for the thermophysical properties of air and mixtures of nitrogen, argon, and oxygen has been a continuing project at the Center for Applied Thermodynamic Studies at the University of Idaho and the National Institute of Standards and Technology (NIST) for more than 10 years [1]. Atmospheric air is a mixture of fluids, including nitrogen, oxygen, argon, carbon dioxide, water vapor, and other trace elements. Standard air is usually assumed to be dry and contains no carbon dioxide or trace elements.

A property formulation is a set of equations used to calculate properties of a fluid at specified thermodynamic states defined by an appropriate number of independent

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Table 1 Summary of prior formulations for the thermodynamic properties of air

Author	Year	Temperature range (K)	High pressure limit (MPa)
Hilsenrath [4]	1955	50–3000	10
Michels et al. [5]	1955	102–348	122
Din [6]	1962	90–450	122
Baehr and Schwier [7]	1961	60–1250	450
Vasserman and Rabinovich [2]	1970	75–160	50
Vasserman et al. [3]	1971	75–1300	100
Sychev et al. [8]	1987	70–1500	100
Jacobsen et al. [9]	1990	60–873	70
Jacobsen et al. [10]	1992	60–873	70
Panasiti et al. [11]	1999	60–2000	2000
Lemmon et al. [1]	2000	59.77–2000	2000

variables. Table 1 shows several previous thermodynamic property formulations for air. Some of them are for liquid states only [2] or vapor states only [3], whereas the others are for both states [1,4–11].

A new equation of state (EoS) for liquids has been recently introduced by Goharshadi et al. [12] (Goharshadi–Morsali–Abbaspour "GMA EoS") which has been found to be valid for polar, nonpolar, and hydrogen-bonded fluids [12–15]. The EoS has also been applied for liquid mixtures [16,17]. The equation of state is based on the average potential energy and is expressed as

$$(2Z - 1)\,V_{\mathrm{m}}^{3} = A(T) + B(T)\rho \tag{1}$$

where Z, V_{m}, and ρ are the compressibility factor, molar volume, and density, respectively. The intercept and slope of this equation depend on temperature via the equations:

$$A(T) = A_0 - \frac{2A_1}{RT} + \frac{2A_2 \ln T}{R} \tag{2}$$

$$B(T) = B_0 - \frac{2B_1}{RT} + \frac{2B_2 \ln T}{R} \tag{3}$$

where $A_0 - A_2$ and $B_0 - B_2$ are constants. To use the equation of state for a liquid, the A and B parameters must be known. To find these parameters, we may plot $(2Z-1)\,V_{\mathrm{m}}^{3}$ versus ρ for different isotherms. The slope and intercept of the straight lines can be fitted to Eqs. 2 and 3 from which $A_0 - A_2$ and $B_0 - B_2$ can be found, respectively.

In the present work, we used the GMA EoS to accurately reproduce and predict the volumetric and thermodynamic properties of air as a pseudo-pure fluid at various temperatures and pressures and compared the results with tabulated data [1]. In addition, we used a model for calculating the thermodynamic properties of nitrogen–oxygen–argon ternary mixtures and nitrogen–oxygen binary mixtures using mixing and combining rules and investigated the validity of assuming air as a ternary mixture or as a binary mixture. The normalized values for the composition of air in mole fractions are 0.7812 nitrogen, 0.2096 oxygen, and 0.0092 argon based upon assuming air as a ternary mixture [9] and 0.7885 nitrogen and 0.2115 oxygen if we assume air as a binary mixture [9].

2 GMA Parameters of Dense Fluid Mixtures

The function used for calculating the density of liquid mixtures from the GMA EoS is given as

$$B(T, x)\rho^5 + A(T, x)\rho^4 + \rho - \frac{2P}{RT} = 0 \tag{4}$$

The parameters A and B can be computed using the quadratic mixing rules that, for a binary mixture, are as follows [16]:

$$A = A_{11}x_1^2 + 2A_{12}x_1x_2 + A_{22}x_2^2 \tag{5}$$

$$B = B_{11}x_1^2 + 2B_{12}x_1x_2 + B_{22}x_2^2 \tag{6}$$

The parameters A_{11}, A_{22}, B_{11}, and B_{22} can be obtained from experimental $P-V-T$ data of pure fluids. The simplest way to compute the parameters A_{12} and B_{12} is to use the combining rules. The most common such rules are the mean geometric rules. They are [17]

$$A_{12} = (A_{11}A_{22})^{1/2} \tag{7}$$

$$B_{12} = (B_{11}B_{22})^{1/2} \tag{8}$$

These equations are known as the "mean geometric approximation" or "MGA." The parameters of the GMA EoS for a ternary mixture can be written as [17]

$$\begin{aligned} A = {} & x_1^2A_{11} + 2x_1x_2\sqrt{A_{11}A_{22}} + x_2^2A_{22} + 2x_1x_3\sqrt{A_{11}A_{33}} + x_3^2A_{33} \\ & + 2x_2x_3\sqrt{A_{22}A_{33}} \end{aligned} \tag{9}$$

$$\begin{aligned} B = {} & x_1^2B_{11} + 2x_1x_2\sqrt{B_{11}B_{22}} + x_2^2B_{22} + 2x_1x_3\sqrt{B_{11}B_{33}} + x_3^2B_{33} \\ & + 2x_2x_3\sqrt{B_{22}B_{33}} \end{aligned} \tag{10}$$

Hence, a knowledge of pure components is enough to determine the parameters of the equation of state for a binary mixture or a ternary mixture.

3 Results and Discussion

3.1 Experimental Test of GMA EoS

We have used the tabulated PVT data of air [1] at various temperatures and pressures to examine the linearity of $(2Z-1)V_m^3$ versus ρ (Eq. 1). Figure 1 shows the results at different temperatures. As the figure shows, the linearity holds well, the slope and the intercept both depend on the temperature. Figure 1 and the values of R^2 in Table 2 show the linearity of $(2Z-1)V_m^3$ versus ρ holds well for air at different temperatures. Table 3 shows the intercept (A), slope (B), and square of the correlation coefficient (R^2) of Eq. 1 for nitrogen, oxygen, and argon. Table 4 shows the values of the constants of Eqs. 2 and 3 for air, nitrogen, oxygen, and argon.

Liquid densities can be calculated from equations of state. The density of air at different temperatures and pressures has been calculated using the GMA EoS by Eq. 4. The percent deviations between the tabulated density data [1] and those calculated with the GMA EoS are presented in Fig. 2. Also, the ability of this EoS to reproduce and predict densities at different temperatures and pressures may be evaluated using statistical parameters [18,19], namely, the absolute average deviation (AAD), the average percent deviation (bias), the root-mean-square deviation (RMSD), and the standard deviation (σ). The AAD is defined as follows:

$$\text{AAD} = \frac{1}{N}\sum_{i=1}^{N} 100\left|\frac{\rho_{\text{exp}}-\rho_{\text{cal}}}{\rho_{\text{exp}}}\right| \tag{11}$$

The statistical parameters between tabulated [1] and calculated densities and the number of points for air as a pseudo-pure fluid, as a ternary mixture, and as a binary mixture are listed in Table 5. This table shows that the GMA EoS can reproduce and predict tabulated densities [1] with good accuracy. Since we can predict the

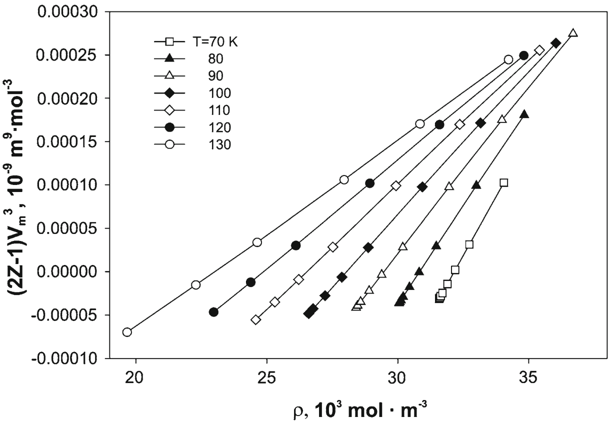

Fig. 1 Isotherms of $(2Z-1)V_m^3$ versus ρ for liquid air

Table 2 Intercept (A), slope (B), and square of correlation coefficient (R^2) of Eq. 1 for air as a pseudo-pure fluid

T (K)	$-A(T)$ $(10^{-9}\,\mathrm{m}^9\cdot\mathrm{mol}^{-3})$	$B(T)\times 10^5$ $(10^{-12}\,\mathrm{m}^{12}\cdot\mathrm{mol}^{-4})$	R^2
60	0.00221878	6.63335	1.0000
66	0.00192114	5.87938	1.0000
72	0.00169036	5.29995	0.9997
78	0.00147539	4.74376	1.0000
84	0.00130133	4.29511	1.0000
90	0.00114679	3.89065	0.9999
96	0.00101545	3.54674	0.9999
102	0.000899746	3.24150	0.9999
108	0.000796801	2.96801	0.9999
114	0.000702182	2.71219	0.9998
120	0.000618600	2.48681	0.9998
126	0.000539621	2.26855	0.9998
132	0.000466768	2.06555	0.9996

properties of air using the knowledge of its pure components, it is plausible to say that the assumption of air as a binary mixture or as a ternary mixture is valid.

We assessed the performance of the GMA EoS compared with other methods, namely, Blanke [20], Michels et al. [21], and Vasserman et al. [22]. The RMSD between the tabulated density data [1] and those predicted using several other methods for air as a pseudo-pure fluid and the numbers of points are given in Table 6.

3.2 Derived Properties

The isobaric expansion coefficient, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, isothermal compressibility, $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$, and internal pressure, $P_i = \left(\frac{\partial U}{\partial V}\right)_T$ and the difference between the isobaric and isochoric heat capacities, $C_P - C_V$, can be calculated at different temperatures and pressures. The functions used for calculating these properties using the GMA EoS are given below:

$$\alpha = \frac{(2B_1+2B_2T)\ \rho^5+(2A_1+2A_2T)\ \rho^4+2P}{5\rho^5\left(RT^2B_0-2B_1T+2T^2B_2\ln T\right)+4\rho^4\left(A_0RT^2-2A_1T+2A_2T^2\ln T\right)+RT^2\rho} \tag{12}$$

$$\kappa_T = \frac{2}{\rho RT+4\rho^4\left(RTA_0-2A_1+2TA_2\ln T\right)+5\rho^5\left(B_0RT-2B_1+2B_2T\ln T\right)} \tag{13}$$

Table 3 Intercept (A), slope (B), and square of correlation coefficient (R^2) of Eq. 1 for nitrogen, oxygen, and argon

T (K)	$-A(T)$ ($10^{-9}\,m^9 \cdot mol^{-3}$)	$B(T) \times 10^5$ ($10^{-12}\,m^{12} \cdot mol^{-4}$)	R^2
Nitrogen			
88	0.00125998	0.0000448791	1.0000
96	0.00106363	0.0000395210	1.0000
104	0.00089821	0.0000349637	1.0000
112	0.00075651	0.0000310237	0.9999
120	0.00063205	0.0000275270	0.9999
124	0.00057509	0.0000259191	0.9998
Oxygen			
88	0.000955862	0.0000259654	1.0000
96	0.000827203	0.0000231355	1.0000
104	0.000718803	0.0000207303	1.0000
112	0.000625677	0.0000186430	1.0000
120	0.000544932	0.0000168158	1.0000
124	0.000508532	0.0000159866	1.0000
Argon			
88	0.000954489	0.0000267353	1.0000
96	0.0008258	0.0000238344	1.0000
104	0.000716869	0.0000213550	1.0000
112	0.000626208	0.0000192944	0.9999
120	0.000542331	0.0000173290	0.9999
124	0.000505542	0.0000164700	0.9999

Table 4 Values of the constants of the GMA EoS (Eqs. 2 and 3) for nitrogen, oxygen, argon, and air as a pseudo-pure fluid

	Air	Nitrogen	Oxygen	Argon
A_0 ($10^{-9}\,m^9 \cdot mol^{-3}$)	0.0007839690	0.0006188690	0.0006898560	0.0003237790
A_1 ($10^{-7}\,m^{12} \cdot Pa \cdot mol^{-4}$)	0.0077414500	0.0081425600	0.0056419400	0.0053791200
A_2 ($10^{-7}\,m^{12} \cdot Pa \cdot mol^{-4} \cdot K^{-1}$)	0.0000014819	0.0000034538	−0.000000762	0.0000019384
R^2	1.0000	1.0000	1.0000	1.0000
B_0 ($10^{-12}\,m^{12} \cdot mol^{-4}$)	0.0000277616	0.0000315125	0.00000915265	0.0000192801
B_1 ($10^{-10}\,m^{15} \cdot Pa \cdot mol^{-5}$)	−0.0001761370	−0.000196296	−0.0001108570	−0.000106570
B_2 ($10^{-10}\,m^{15} \cdot Pa \cdot mol^{-5} \cdot K^{-1}$)	−0.0000003323	−0.000000376	−0.0000001270	0.0000002021
R^2	1.0000	1.0000	1.0000	0.9999

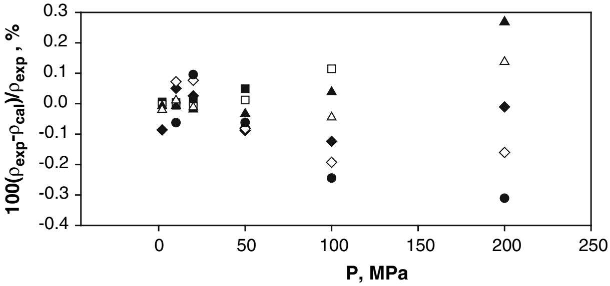

Fig. 2 Percent deviation between the tabulated density data [1] and those calculated with the GMA EoS for air as a pseudo-pure fluid at different temperatures: ■ 70 K; □ 80 K; ▲ 90 K; △ 100 K; ◆ 110 K; ◇ 120 K; ● 130 K

Table 5 Statistical parameters between tabulated [1] and calculated densities, and the number of points for air as a pseudo-pure fluid, as a ternary mixture, and as a binary mixture

Parameter	Air as a pseudo-pure fluid	Air as a ternary mixture	Air as a binary mixture
Bias (%)	−0.028	0.856	−0.277
AAD (%)	0.058	0.856	1.209
RMSD (%)	0.107	0.921	1.529
σ (10^3 mol · m^{-3})	0.031	0.249	0.487
NP	295	76	76

Table 6 Root-mean-square deviation (RMSD) between tabulated density data and those predicted using several methods for air as a pseudo-pure fluid

Reference	RMSD	No. of points
Blanke [20]	0.043605	49
Michels et al. [21]	0.230804	8
Vasserman et al. [22]	0.066310	87
This work	0.107134	295

$$P_i = (B_1 + B_2 T)\,\rho^5 + (A_1 + A_2 T)\,\rho^4 \tag{14}$$

$$C_p - C_v = \frac{T\alpha^2}{\kappa_T \rho} \tag{15}$$

As far as the authors are aware, there are no corresponding tabulated data to which the present calculations of α_P, κ_T, and P_i can be compared. Just for $C_P - C_V$ the comparison of tabulated values [1] with those calculated using Eq. 15 has been made. The bias and AAD are 1.81% and 2.59%, respectively.

4 Conclusion

We have developed a new equation of state called the GMA EoS and applied it to liquid air. We have found that the GMA EoS calculates thermodynamic properties of air successfully and accurately. The capability of this EoS to predict densities has been demonstrated and compared with several other methods. It can also predict other volumetric and thermodynamic properties of air at any temperature and pressure. Also, we used the GMA EoS to predict the density of air at different temperatures and pressures with air as a ternary mixture or as a binary mixture. The results show these assumptions are valid. In general, the GMA EoS provides a simple procedure for prediction of thermodynamic properties of air.

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