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Research Article

Thermodynamic and Thermophysical Properties of Air as a Mixture by Using Schreiber-Pitzer EoS

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Abstract

Air is one of the most important substances used in industrial and technological applications. Applications of air require a consistent set of reliable data on its thermodynamic and thermophysical properties. Over the last few decades, researchers have developed a number of empirical and theoretical models for the correlation and prediction of the thermodynamic and thermophysical properties of pure fluids and mixtures. The ideal gas Equation of State (EoS) is used in gas thermodynamic property calculations extensively, but in applications with higher pressure zones, the error levels are increasing. For most applications, an equation of state with better accuracy of thermodynamic properties will be required for extreme cases. In this study, Schreiber-Pitzer EoS is considered for better accuracy of the thermodynamic properties for air mixture. A set of computer programs were developed in java language to calculate the thermodynamic and thermophysical properties of air as a mixture of Nitrogen, Oxygen and Argon. The Schreiber-Pitzer EoS results are compared with Peng-Robinson EoS, Redlich-Kwong EoS, Van der Waals EoS, and ideal gas EoS utilizing cubic spline curve fitting for c_p values. The thermodynamic and thermophysical property results and percentages of differences are calculated. The percentages of differences are increasing with increasing pressure and decreasing temperature.

Keywords: *Schreiber-Pitzer EoS; thermodynamic properties of air; thermophysical properties of air; cubic spline.*

1. Introduction

Accurate knowledge of the thermodynamic properties of gases and mixtures is needed for efficient design and operating processes. A variety of equations of state are available in the literature. The simplest and best known equation of state for substances in the gas phase is the ideal gas EoS, but its range of applicability is limited. The first cubic equation of state was proposed by J. D. Van der Waals in 1873 [1,2]. Van der Waals intended to improve the ideal gas EoS by including two of the effects not considered in the ideal gas model: the intermolecular attraction forces and the volume occupied by the molecules themselves. Redlich Kwong EoS, which is a considerably more accurate cubic equation than Van der Waals, was proposed in 1949 [3]. Cubic equations of state are rather simple and easy to extend to new components because only a few substance specific parameters are needed. They are accurate enough for high pressure applications. The Peng-Robinson EoS, which was suggested by Ding-Yu Peng and Donald B. Robinson in 1976, achieves simple and accurate predictions [4,5]. Peng-Robinson EoS has been widely used in thermodynamic calculations in industrial and scientific studies since 1976 [6]. Some of the researchers discussed the Peng-Robinson EoS in depth [7,8]. Zabaloy and Vera in 1998 compared Peng-Robinson EoS with other equations of state. They found, that Peng-Robinson EoS was clearly superior to the other forms considered in their study [9]. Valderrama gave general recommendations for using the Peng-Robinson EoS for reliable application [10].

Schreiber-Pitzer EoS utilizes Pitzer's acentric factor, which is a modified form of Benedict-Webb-Rubin EoS [11]. It is basically a quadratic curve fitting equation to reference fluids by using Pitzer's acentric factor as a variable. A rich list of curve fitting reference fluids, including hydrocarbons and other gases, is used to obtain curve fitting coefficients of the EoS. In this study, specific heat values are added into the program as cubic spline curve fitting values. In order to create actual data for specific heat data, it is assumed that air is a mixture of Nitrogen, Oxygen and Argon. By getting specific heat and critical properties of these gases, pseudocritical properties of air are calculated and used as input parameters to Schreiber-Pitzer EoS. The Schreiber-Pitzer EoS results are compared with Peng-Robinson EoS, Redlich-Kwong EoS, Van der Waals EoS, and ideal gas EoS. The property results and percentages of differences are given and interpreted.

2. Theory

2.1 Formulation of EoS and Thermodynamic Properties

In this paper, the Schreiber-Pitzer equation of state was considered for air as a mixture of Nitrogen, Oxygen and Argon. The specific heat and the pseudocritical properties of air are calculated from the critical properties of the gases and used as input parameters to the Schreiber-Pitzer EoS. Details of the Schreiber-Pitzer EoS is given in Eq. (1).

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$$Z = \frac{P}{\rho RT} = 1 + B(T_r, \rho_r)\rho_r + C(T_r, \rho_r)\rho_r^2 + D(T_r, \rho_r)\rho_r^3 + E(T_r, \rho_r)\rho_r^5 + F(T_r, \rho_r)\rho_r^7 + G(T_r, \rho_r)\rho_r^8 + H(T_r, \rho_r)\rho_r^{10} + I(T_r, \rho_r)\rho_r^{12} \quad (1)$$

$$B(T_r, \rho_r) = c_1 + \frac{c_2}{T_r} + \frac{c_3}{T_r^2} + \frac{c_4}{T_r^6} \quad (2)$$

$$C(T_r, \rho_r) = c_5 + \frac{c_6}{T_r} + \frac{c_7}{T_r^3} + \frac{c_8}{T_r^4}\exp(-\rho_r^2) \quad (3)$$

$$D(T_r, \rho_r) = c_9 + \frac{c_{10}}{T_r} + \frac{c_{11}}{T_r^2} \quad (4)$$

$$E(T_r, \rho_r) = \frac{c_{12}}{T_r^2} + \frac{c_{13}}{T_r^3} \quad (5)$$

$$F(T_r, \rho_r) = \frac{c_{14}}{T_r^2} + \frac{c_{15}}{T_r^3} \quad (6)$$

$$G(T_r, \rho_r) = \frac{c_{16}}{T_r^3} + \left(\frac{c_{17}}{T_r^3} + \frac{c_{18}}{T_r^5}\right)\exp(-\rho_r^2) \quad (7)$$

$$H(T_r, \rho_r) = \left(\frac{c_{19}}{T_r^3} + \frac{c_{20}}{T_r^4}\right)\exp(-\rho_r^2) \quad (8)$$

$$I(T_r, \rho_r) = \left(\frac{c_{21}}{T_r^3} + \frac{c_{22}}{T_r^4}\right)\exp(-\rho_r^2) \quad (9)$$

$$c_i = C_{i,0} + C_{i,1}\omega + C_{i,2}\omega^2 \quad (10)$$

"ω" coefficient is called Pitzer's acentric factor in Schreiber-Pitzer EoS. Acentric factor is given in Eq. (11).

$$\omega = -log_{10} P_{saturated\ vapor}(at\ T_r = 0.7) - 1 \quad (11)$$

The coefficients of Schreiber-Pitzer EoS in Eq. (10) are given in Table 1.

Table 1. Coefficients ($c_{i,j}$) of Schreiber-Pitzer EoS.

	j=1	j=2	j=3
$C_{1,j}$	0.4422590000	0.7256500000	0.0000000000
$C_{2,j}$	-0.9809700000	0.2187140000	0.0000000000
$C_{3,j}$	-0.6111420000	-1.2497600000	0.0000000000
$C_{4,j}$	-0.0051562400	-0.1891870000	0.0000000000
$C_{5,j}$	0.1513654000	2.3067060000	-10.4117400000
$C_{6,j}$	-0.0438262500	4.6960680000	15.1414600000
$C_{7,j}$	1.1026990000	3.1293840000	-9.5214090000
$C_{8,j}$	-0.6361056000	0.3266766000	2.9046220000
$C_{9,j}$	0.0087596260	-3.2040990000	8.0023380000
$C_{10,j}$	0.3412103000	8.8721690000	-14.4038600000
$C_{11,j}$	-0.8842722000	-6.6874710000	11.7685400000
$C_{12,j}$	0.1375109000	0.2432806000	-0.5515101000
$C_{13,j}$	-0.1443457000	1.2869320000	-2.1809880000
$C_{14,j}$	-0.0059695540	0.0454196100	0.0000000000
$C_{15,j}$	0.0245053700	-0.4158241000	0.7914067000
$C_{16,j}$	-0.0041995900	0.0910596000	-0.1786378000
$C_{17,j}$	0.0004665477	-1.2620280000	-2.8267720000
$C_{18,j}$	-0.0194510100	0.7812220000	4.1900460000
$C_{19,j}$	0.0408364300	1.3988440000	0.0000000000
$C_{20,j}$	-0.0354691700	-1.4560410000	0.0000000000
$C_{21,j}$	-0.0028779550	0.2104505000	0.0000000000
$C_{22,j}$	0.0058962650	0.2191255000	0.0000000000

Derivatives of the Eq. (1) are given in the Eqs. (12)-(26).

$$\frac{\partial B(T_r,\rho_r)}{\partial T} = \frac{1}{T_c}\left[-\frac{c_2}{T_r^2} - 2\frac{c_3}{T_r^3} - 6\frac{c_4}{T_r^7}\right] \quad (12)$$

$$\frac{\partial C(T_r,\rho_r)}{\partial T} = \frac{1}{T_c}\left[-\frac{c_6}{T_r^2} - 3\frac{c_7}{T_r^4} - 4\frac{c_8}{T_r^5}\exp(-\rho_r^2)\right] \quad (13)$$

$$\frac{\partial D(T_r,\rho_r)}{\partial T} = \frac{1}{T_c}\left[-\frac{c_{10}}{T_r^2} - 2\frac{c_{11}}{T_r^3}\right] \quad (14)$$

$$\frac{\partial E(T_r,\rho_r)}{\partial T} = \frac{1}{T_c}\left[-2\frac{c_{12}}{T_r^3} - 3\frac{c_{13}}{T_r^4}\right] \quad (15)$$

$$\frac{\partial F(T_r,\rho_r)}{\partial T} = \frac{1}{T_c}\left[-2\frac{c_{14}}{T_r^3} - 3\frac{c_{13}}{T_r^4}\right] \quad (16)$$

$$\frac{\partial G(T_r,\rho_r)}{\partial T} = \frac{1}{T_c}\left[-3\frac{c_{16}}{T_r^4} + \left(-3\frac{c_{17}}{T_r^4} - 5\frac{c_{18}}{T_r^6}\right)\exp(-\rho_r^2)\right] \quad (17)$$

$$\frac{\partial H(T_r,\rho_r)}{\partial T} = \frac{1}{T_c}\left[\left(-3\frac{c_{19}}{T_r^4} - 4\frac{c_{20}}{T_r^5}\right)\exp(-\rho_r^2)\right] \quad (18)$$

$$\frac{\partial I(T_r,\rho_r)}{\partial T} = \frac{1}{T_c}\left[\left(-3\frac{c_{21}}{T_r^4} - 4\frac{c_{22}}{T_r^5}\right)\exp(-\rho_r^2)\right] \quad (19)$$

$$\frac{\partial B(T_r,\rho_r)}{\partial \rho} = \frac{\partial D(T_r,\rho_r)}{\partial \rho} = \frac{\partial E(T_r,\rho_r)}{\partial \rho} = \frac{\partial F(T_r,\rho_r)}{\partial \rho} = 0 \quad (20)$$

$$\frac{\partial C(T_r,\rho_r)}{\partial \rho} = \frac{1}{\rho_c}\left[-2\rho_r\frac{c_8}{T_r^4}\exp(-\rho_r^2)\right] \quad (21)$$

$$\frac{\partial G(T_r,\rho_r)}{\partial \rho} = \frac{1}{\rho_c}\left[-2\rho_r\left(\frac{c_{17}}{T_r^3} + \frac{c_{18}}{T_r^5}\right)\exp(-\rho_r^2)\right] \quad (22)$$

$$\frac{\partial H(T_r,\rho_r)}{\partial \rho} = \frac{1}{\rho_c}\left[-2\rho_r\left(\frac{c_{19}}{T_r^3} + \frac{c_{20}}{T_r^4}\right)\exp(-\rho_r^2)\right] \quad (23)$$

$$\frac{\partial I(T_r,\rho_r)}{\partial \rho} = \frac{1}{\rho_c}\left[-2\rho_r\left(\frac{c_{21}}{T_r^3} + \frac{c_{22}}{T_r^4}\right)\exp(-\rho_r^2)\right] \quad (24)$$

$$\left.\frac{\partial P(T_r,\rho_r)}{\partial T}\right|_\rho = \rho RT\left[\frac{\partial B(T_r,\rho_r)}{\partial T}\rho_r + \frac{\partial C(T_r,\rho_r)}{\partial T}\rho_r^2 + \frac{\partial D(T_r,\rho_r)}{\partial T}\rho_r^3 + \frac{\partial E(T_r,\rho_r)}{\partial T}\rho_r^5 + \frac{\partial F(T_r,\rho_r)}{\partial T}\rho_r^7 + \frac{\partial G(T_r,\rho_r)}{\partial T}\rho_r^8 + \frac{\partial H(T_r,\rho_r)}{\partial T}\rho_r^{10} + \frac{\partial I(T_r,\rho_r)}{\partial T}\rho_r^{12}\right] + \rho R[1 + B(T_r,\rho_r)\rho_r + C(T_r,\rho_r)\rho_r^2 + D(T_r,\rho_r)\rho_r^3 + E(T_r,\rho_r)\rho_r^5 + F(T_r,\rho_r)\rho_r^7 + G(T_r,\rho_r)\rho_r^8 + H(T_r,\rho_r)\rho_r^{10} + I(T_r,\rho_r)\rho_r^{12}] \quad (25)$$

$$\left.\frac{\partial P(T_r,\rho_r)}{\partial \rho}\right|_T = RT[1 + B(T_r,\rho_r)\rho_r + C(T_r,\rho_r)\rho_r^2 + D(T_r,\rho_r)\rho_r^3 + E(T_r,\rho_r)\rho_r^5 + F(T_r,\rho_r)\rho_r^7 + G(T_r,\rho_r)\rho_r^8 + H(T_r,\rho_r)\rho_r^{10} + I(T_r,\rho_r)\rho_r^{12}] + \rho RT\left[\frac{\partial C(T_r,\rho_r)}{\partial \rho}\rho_r^2 + \frac{\partial G(T_r,\rho_r)}{\partial \rho}\rho_r^8 + \frac{\partial H(T_r,\rho_r)}{\partial \rho}\rho_r^{10} + \frac{\partial I(T_r,\rho_r)}{\partial \rho}\rho_r^{12}\right] + RT[B(T_r,\rho_r)\rho_r + 2C(T_r,\rho_r)\rho_r^2 + 3D(T_r,\rho_r)\rho_r^3 + 5E(T_r,\rho_r)\rho_r^5 + 7F(T_r,\rho_r)\rho_r^7 + 8G(T_r,\rho_r)\rho_r^8 + 10H(T_r,\rho_r)\rho_r^{10} + 12I(T_r,\rho_r)\rho_r^{12}] \quad (26)$$

The Helmholtz energy equation is given in Eq. (27).

$$dA = \left(\frac{\partial A(T,v)}{\partial T}\right)_v dT + \left(\frac{\partial A(T,v)}{\partial v}\right)_T dv \quad (27)$$

$$dA = -sdT - Pdv \quad (28)$$

$$\left.\frac{\partial A}{\partial v}\right|_T = -P \quad (29)$$

$$dA = -Pdv = \frac{P}{\rho^2}d\rho \quad (30)$$

$$A - A_0 = \int_{\rho_0}^{\rho} \frac{P}{\rho^2} d\rho = \int_0^{\rho} \frac{P}{\rho^2} d\rho + \int_{\rho_0}^{0} \frac{P}{\rho^2} d\rho$$

$$= \int_0^{\rho} \frac{P}{\rho^2} d\rho + \int_{\rho_0}^{0} \frac{\rho RT}{\rho^2} d\rho \qquad (31)$$

The second term (limits between low density ρ_0 and zero density) can be defined as an ideal state case where $P=\rho RT$. After adding and subtracting the ideal gas density term, the equation can be written as Eq. (32).

$$A - A_0 = \int_0^{\rho} \frac{P}{\rho^2} d\rho + \int_{\rho_0}^{0} \frac{\rho RT}{\rho^2} d\rho$$

$$+ \int_0^{\rho} \frac{\rho RT}{\rho^2} d\rho - \int_0^{\rho} \frac{\rho RT}{\rho^2} d\rho \qquad (32)$$

Considering the equation $P=Z\rho RT$ for real EoS, Eq. (33) is obtained.

$$A - A_0 = \int_0^{\rho} \frac{Z\rho RT - \rho RT}{\rho^2} d\rho + \int_{\rho_0}^{\rho} \frac{\rho RT}{\rho^2} d\rho \qquad (33)$$

$$A - A_0 = \int_0^{\rho} \frac{RT(Z-1)}{\rho} d\rho + \int_{\rho_0}^{\rho} \frac{\rho RT}{\rho^2} d\rho \qquad (34)$$

$$A - A_0 = \int_0^{\rho_r} \frac{1}{\rho_r} d\rho_r + \int_{\rho_{r0}}^{\rho_r} \frac{RT}{\rho_r} d\rho_r \qquad (35)$$

$$A - A_0 = RT \int_0^{\rho_r} [B(T_r, \rho_r) + C(T_r, \rho_r)\rho_r + D(T_r, \rho_r)\rho_r^2 + E(T_r, \rho_r)\rho_r^4 + F(T_r, \rho_r)\rho_r^6 + G(T_r, \rho_r)\rho_r^7 + H(T_r, \rho_r)\rho_r^9 + I(T_r, \rho_r)\rho_r^{11}] d\rho_r + RTln \frac{\rho_r}{\rho_{r0}} \qquad (36)$$

The terms in Eq. (36) include exponential and power multiplication terms. The integration can be carried out as Eq. (37).

$$K(m, \rho_r) = \int_0^{\rho_r} \rho_r^m \exp(-\rho_r^2)\, d\rho_r = \int_0^{\rho_r} \sum_{n=0}^{\infty} (-1)^n \frac{\rho_r^{2n+m}}{n!} d\rho_r = \sum_{n=0}^{\infty} (-1)^n \frac{\rho_r^{2n+m+1}}{(2n+m+1)n!} \qquad (37)$$

It is easier to take the Taylor series than take numerical integrals. The Helmholtz energy equation can be written as Eq. (38).

$$A - A_0 = RT\left(B\rho_r + C_1 \frac{\rho_r^2}{2} + C_2 K(1, \rho_r) + D\frac{\rho_r^3}{3} + E\frac{\rho_r^5}{5} + F\frac{\rho_r^7}{7} + G_1 \frac{\rho_r^8}{8} + G_2, K(8, \rho_r) + H_2 K(10, \rho_r) + I_2 K(12, \rho_r)\right) + RTln\left(\frac{\rho_r}{\rho_{r0}}\right) \qquad (38)$$

Entropy function is given in Eqs. (39) and (40).

$$s - s_0 = -\frac{\partial(A - A_0)}{\partial T}\bigg|_{\rho} \qquad (39)$$

$$s - s_0 = R\left(B\rho_r + C_1 \frac{\rho_r^2}{2} + C_2 K(1, \rho_r) + D\frac{\rho_r^3}{3} + E\frac{\rho_r^5}{5} + F\frac{\rho_r^8}{8} + G_1 \frac{\rho_r^9}{9} + G_2, K(8, \rho_r) + H_2 K(10, \rho_r) + I_2 K(12, \rho_r)\right) + RT\left(\frac{dB}{dT}\rho_r + \frac{dC_1}{dT}\frac{\rho_r^2}{2} + \frac{dC_2}{dT} K(1, \rho_r) + \frac{dD}{dT}\frac{\rho_r^3}{3} + \frac{dE}{dT}\frac{\rho_r^5}{5} + \frac{dF}{dT}\frac{\rho_r^8}{8} + \frac{dG_1}{dT}\frac{\rho_r^9}{9} + \frac{dG_2}{dT} K(8, \rho_r) + \frac{dH_2}{dT} K(10, \rho_r) + \frac{dI_2}{dT} K(12, \rho_r)\right) + Rln\left(\frac{\rho_r}{\rho_{r0}}\right) \qquad (40)$$

Internal energy function is expressed as Eq. (41).

$$u - u_0 = (A - A_0) + T(S - S_0) \qquad (41)$$

Enthalpy energy function can be evaluated as Eq. (42).

$$h - h_0 = (A - A_0) + T(S - S_0) + RT(Z - 1) \qquad (42)$$

Gibbs energy function is given in Eq. (43).

$$G - G_0 = (A - A_0) + RT(Z - 1) \qquad (43)$$

The fugacity-pressure ratio can be evaluated as Eq. (44).

$$ln\frac{f}{P} = \frac{(A - A_0)}{RT} + ln\frac{v}{v_0} + (Z - 1) - \ln(Z) \qquad (44)$$

Thermodynamic properties of air are calculated by assuming air as a gas mixture of Nitrogen, Oxygen, and Argon. The air mixture ratios are given in Table 2.

Table 2. Air mixture ratios.

Gas	Formula	Mole (%)	Molar mass, M (kg/kmol)
Nitrogen	N_2	0.78112	28.014
Oxygen	O_2	0.20954	31.998
Argon	Ar	0.00934	39.948
Air		1	28.96029

The NIST-JANAF tables are used to solve the $c_p(T)$ for air as a mixture of Nitrogen, Oxygen, and Argon [12]. Mixing rule is applied to establish $c_p(T)$ of air which was given in Eq. (45).

$$c_{p,air}(T) = N_{N2}c_{p,N2}(T) + N_{O2}c_{p,O2}(T) + N_{Ar}c_{p,Ar}(T) \qquad (45)$$

In this paper, cubic spline interpolation is used to calculate the $c_p(T)$ values. In the cubic spline interpolation, a third-degree polynomial equation is considered, which is given in Eq. (46).

$$s_k(x) = a_k(x - x_k) + b_k(x_{k+1} - x) + \frac{[(x - x_k)^3 c_{k+1} + (x_{k+1} - x)^3 c_k]}{6h_k}$$

$$1 \le k \le n \qquad (46)$$

The first and second derivative of the third-degree polynomial is given in Eq. (47) and Eq. (48).

$$h_k = x_{k+1} - x_k \quad 1 \le k \le n$$

$$s'_k(x) = a_k - b_k + \frac{[(x - x_k)^2 c_{k+1} - (x_{k+1} - x)^2 c_k]}{2h_k} \qquad (47)$$

$$s''_k(x) = \frac{[(x - x_k)c_{k+1} - (x_{k+1} - x)c_k]}{h_k} \qquad (48)$$

The equations are evaluated through additional rules.

$$S_k(x_k) = y_k \quad (49)$$

$$S_k(x_{k+1}) = y_{k+1} \quad (50)$$

$$S_k(x_k) = y_k = b_k(x_{k+1} - x_k) + \left[\frac{(x_{k+1}-x_k)^3}{6h_k} C_k\right] = \left[b_k h_k + \frac{{h_k}^3}{6h_k} C_k\right] \quad (51)$$

$$S_k(x_{k+1}) = y_{k+1} = a_k(x_{k+1} - x_k) + \left[\frac{(x_{k+1} - x_k)^3}{6h_k} C_{k+1}\right] = a_k h_k + \left[\frac{{h_k}^3}{6h_k} C_{k+1}\right] \quad (52)$$

The "a_k" and "b_k" coefficients can be evaluated as Eqs. (53) and (54).

$$a_k = \frac{[6y_{k+1} - h_k^2 c_{k+1}]}{6h_k} \quad 1 \le k \le n \quad (53)$$

$$b_k = \frac{[6y_k - h_k^2 c_k]}{6h_k} \quad 1 \le k \le n \quad (54)$$

The equations are evaluated considering the boundary conditions.

$$S'_{k-1}(x_k) = S'_k(x_k) \quad (55)$$

$$S'_k(x_k) = a_k - b_k - \left[\frac{(x_{k+1}-x_k)^2}{2h_k} C_k\right] = a_k - b_k \left[\frac{{h_k}^2}{2h_k} C_k\right] \quad (56)$$

$$S'_{k-1}(x_k) = a_{k-1} - b_{k-1} + \left[\frac{(x_k - x_{k-1})^2}{2h_{k-1}} C_k\right] = a_{k-1} - b_{k-1} + \left[\frac{{h_{k-1}}^2}{2h_{k-1}} C_k\right] \quad (57)$$

$$a_k - b_k - \left[\frac{h_k}{2} C_k\right] = a_{k-1} - b_{k-1} + \left[\frac{h_{k-1}}{2} C_k\right] \quad (58)$$

$$\left[\frac{6y_{k+1} - {h_k}^2 C_{k+1}}{6h_k}\right] - \left[\frac{6y_k - {h_k}^2 C_k}{6h_k}\right] - \left[\frac{h_k}{2} C_k\right] = \left[\frac{6y_k - {h_{k-1}}^2 C_k}{6h_{k-1}}\right] - \left[\frac{6y_{k-1} - {h_{k-1}}^2 C_{k-1}}{6h_{k-1}}\right] + \left[\frac{h_{k-1}}{2}\right] C_k \quad (59)$$

Eq. (60) is obtained by deriving from Eq. (59).

$$h_{k-1} C_{k-1} + 2C_k(h_{k-1} + h_k) + h_k C_{k+1} = 6\left[\left[\frac{y_{k+1} - y_k}{h_k}\right] - \left[\frac{y_k - y_{k-1}}{h_{k-1}}\right]\right] \quad (60)$$

The system of equations is given in Eq. (62) with the application of Eq. (61) definition.

$$w_k = \frac{y_{k+1} - y_k}{h_k} = \frac{y_{k+1} - y_k}{x_{k+1} - x_k} \quad 1 \le k \le n \quad (61)$$

$$\begin{bmatrix} 1 & & & & & & \\ h_1 & 2(h_1 + h_2) & h_2 & & & & \\ & h_2 & 2(h_2 + h_3) & & & & \\ & \cdots \;\; \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ & & & \cdots. & 2(h_{n-3} + h_{n-2}) & h_{n-2} & \\ & & & & h_{n-2} & 2(h_{n-2} + h_{n-1}) & h_{n-1} \\ & & & & & & 1 \end{bmatrix} \begin{Bmatrix} c_0 \\ c_1 \\ c_2 \\ \cdots \\ c_{n-2} \\ c_{n-1} \\ c_n \end{Bmatrix} = \begin{Bmatrix} A \\ 6(w_2 - w_1) \\ 6(w_3 - w_2) \\ \cdots \\ 6(w_{n-2} - w_{n-3}) \\ 6(w_{n-1} - w_{n-2}) \\ B \end{Bmatrix} \quad (62)$$

The system of equation has "*n-2*" terms to be solved. In the equation there are second derivative at the end conditions. "*A*" and "*B*" values should be defined by the users. The matrix which is given in Eq. (62) is a band matrix, it can be solved by using band matrix algorithms such as Thomas algorithm or another method. The cubic spline interpolation, which is given above, was used to calculate the $c_p(T)$ values of air as a mixture.

The cubic spline curve fitting for air $c_p(T)$ data is given in Figure 1.

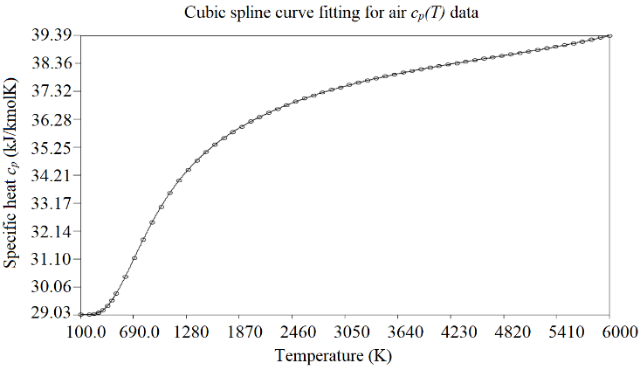

Figure 1. Specific heat of air ($c_p(T)$, kJ/kmolK).

The pseudocritical property approach is used to calculate the gas mixture properties. Mixing rules for Schreiber-Pitzer EoS are given in the equations.

$$N = \sum_i N_i \quad (63)$$

"N_i" is the mole number of each substance in the mixture.

$$y_i = \frac{N_i}{N} \quad (64)$$

"y_i" is the mole percentages of each substance.

Mixture properties can be calculated by assuming pseudocritical values from mixing equations and air is assumed as a single gas instead of gas mixtures [13].

$$T_{cm} = \sum_{i=1}^{m} \sum_{j=1}^{m} y_i y_j T_{cij} \quad (65)$$

$$V_{cm} = \sum_{i=1}^{m} \sum_{j=1}^{m} y_i y_j V_{cij} \quad (66)$$

To calculate the mixture interaction, combination rules must be devised to obtain T_{cij}, P_{cij}, and w_{ij}. Leland and Chappelear [14] and Ramaiah and Stiel [15] investigated the mixture interactions.

$$T_{cij} = \sqrt{T_{ci} T_{cj}}(1 - k_{ij}) \quad (67)$$

$$P_{cij} = \frac{Z_{cij} R T_{cij}}{V_{cij}} \quad (68)$$

$$\omega_{ij} = \frac{1}{2}[\omega_i + \omega_j] \quad (69)$$

$$V_{c\,ij} = \frac{1}{8}\left[(V_{ci})^{\frac{1}{3}} + (V_{cj})^{\frac{1}{3}}\right]^3 \quad (70)$$

$$Z_{cij} = \frac{1}{2}[Z_{ci} + Z_{cj}] \quad (71)$$

"k_{ij}" is the binary interaction coefficient, which is given in Eq. (72). Tsonopoulos [16] investigated the prediction and correlation of interaction coefficients. The guidelines for estimating the interaction coefficients have been given by Tarakad and Danner [17].

$$k_{ij} = 1 - \frac{\left(V_{crit\,ii}V_{crit\,jj}\right)^{\frac{1}{2}}}{V_{crit\,ij}} \tag{72}$$

2.2 Formulation of Thermophysical Properties

The thermophysical properties of air, such as thermal conductivity and viscosity, are calculated with the equations suggested by Kadoya et al [18].

$$\eta(T_r,\rho_r) = H\left[\eta_0(T_r) + \Delta\eta(\rho_r)\right] \tag{73}$$

$$\eta_0(T_r) = A_0T_r + A_1T_r^{0.5} + A_2 + \frac{A_3}{T_r} + \frac{A_4}{T_r^2} + \frac{A_5}{T_r^3} + \frac{A_6}{T_r^4} \tag{74}$$

$$\Delta\eta(\rho_r) = \sum_{i=1}^{4} B_i\rho_r^i \tag{75}$$

$$\mathrm{k}(T_r,\rho_r) = \Lambda[k_0(T_r) + \Delta\mathrm{k}(\rho_r)] \tag{76}$$

$$k_0(T_r) = C_0T_r + C_1T_r^{0.5} + C_2 + \frac{C_3}{T_r} + \frac{C_4}{T_r^2} + \frac{C_5}{T_r^3} + \frac{C}{T_r^4} \tag{77}$$

$$\Delta\mathrm{k}(\rho_r) = \sum_{i=1}^{4} D_i\rho_r^i \tag{78}$$

$$\rho_r = \frac{\rho}{\rho^*} \tag{79}$$

$$T_r = \frac{T}{T^*} \tag{80}$$

In Eq. (73) and Eq. (76) "H" is equal to 6.1609 (10^{-6} Pa), "Λ" is equal to 25.9778 (10^{-3} $W/(mK)$, ρ^* is equal to 314.3 kg/m^3 and T^* is equal to 132.5 K. The coefficients of Eqs. (73) and (76) are given in Table 3.

Table 3. Coefficients of Eq. (73) and Eq. (76).

i	A_i	B_i	C_i	D_i
0	0.128517	0.465601	0.239503	0.402287
1	2.60661	1.26469	0.00649768	0.356603
2	-1	-0.511425	1	-0.163159
3	-0.709661	0.2746	-1.92615	0.138059
4	0.662534		2.00383	-0.0201725
5	-0.197846		-1.07553	
6	0.00770147		0.229414	

Additional properties derived from EoS are given in Table 4.

Table 4. Additional properties derived from EoS.

Properties	Equation
Prandtl number	$Pr = \frac{c_p\mu}{k}$
Speed of sound	$a = \sqrt{-\left(\frac{v^2c_p}{c_vM}\right)\left(\frac{\partial P}{\partial v}\right)_T}$
Thermal expansion coefficient	$\beta = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_P$
Isothermal compressibility	$\beta_T = \sqrt{\frac{v}{\left(\frac{\partial P}{\partial v}\right)_T}}$

3. Results

The Java language is used to carry out the analysis. The list of programs is given in Table 5. The programs are available on the internet web site for free utilization by researchers [19].

Table 5. Java program list.

Java program	Explanation
Interface if_x	The basic interface for the general definition of the function f(x), including derivatives, integrals, and root-finding algorithms.
air_SP_CS	The Schreiber-Pitzer EoS was considered for air, utilizing cubic spline curve fitting for c_p values.
air_PR_CS	The Peng-Robinson EoS was considered for air, utilizing cubic spline curve fitting for c_p values.
air_RK_CS	The Redlich-Kwong EoS was considered for air, utilizing cubic spline curve fitting for c_p values.
air_VDW_CS	The Van der Waals EoS was considered for air, utilizing cubic spline curve fitting for c_p values.
air_PG_CS	The ideal gas EoS was considered for air, utilizing cubic spline curve fitting for c_p values.

Comparisons of five EoS results for air as a mixture are given in Table 6 and the comparisons of additional property results derived from EoS for air are given in Table 7.

Table 6. Comparisons of different EoS results.

EoS	P kPa	T K	v m^3/kg	h kJ/kg	u kJ/kg	s kJ/kgK
Schreiber-Pitzer	100	300	0.861287	200.3428	114.2382	5.842212
Peng-Robinson	100	300	0.860835	200.5240	114.4406	5.842357
Redlich-Kwong	100	300	0.860913	200.4628	114.3715	5.842153
Van der Waals	100	300	0.860681	200.3165	114.2484	5.842157
Ideal gas	100	300	0.861301	200.5688	114.4387	5.842792
Schreiber-Pitzer	500	300	0.172250	199.4418	113.4324	5.377784
Peng-Robinson	500	300	0.171796	200.3461	114.4481	5.378532
Redlich-Kwong	500	300	0.171880	200.0423	114.1022	5.377530
Van der Waals	500	300	0.171646	199.3055	113.4825	5.377539
Ideal gas	500	300	0.172260	200.5688	114.4387	5.380722
Schreiber-Pitzer	1000	300	0.086121	198.3379	112.4311	5.175817
Peng-Robinson	1000	300	0.085668	200.1259	114.4574	5.177331
Redlich-Kwong	1000	300	0.085761	199.5264	113.7659	5.175355
Van der Waals	1000	300	0.085524	198.0427	112.5191	5.175345
Ideal gas	1000	300	0.086130	200.5688	114.4387	5.181719
Schreiber-Pitzer	5000	300	0.017217	190.3800	104.6491	4.689713
Peng-Robinson	5000	300	0.016788	198.4718	114.5311	4.697481
Redlich-Kwong	5000	300	0.016944	195.8235	111.1020	4.688837
Van der Waals	5000	300	0.016695	188.0779	104.6028	4.687668
Ideal gas	5000	300	0.017226	200.5688	114.4387	4.719648

Table 7. Comparisons of additional properties derived from EoS.

EoS	P kPa	T K	Pr	a m/s	β 1/K	β_T 1/Pa
Schreiber-Pitzer	100	300	0.71203	347.2425	0.00333	1E-5
Peng-Robinson	100	300	0.71203	347.0611	0.00333	1E-5
Redlich-Kwong	100	300	0.71203	347.2382	0.00333	1E-5
Van der Waals	100	300	0.71203	347.2176	0.00333	1E-5
Ideal gas	100	300	0.71203	347.2476	0.00333	1E-5
Schreiber-Pitzer	500	300	0.71209	347.2281	0.00333	2E-6
Peng-Robinson	500	300	0.71209	346.3495	0.00333	2E-6
Redlich-Kwong	500	300	0.71209	347.2122	0.00333	2E-6
Van der Waals	500	300	0.71209	347.1212	0.00333	2E-6
Ideal gas	500	300	0.71209	347.2476	0.00333	2E-6
Schreiber-Pitzer	1000	300	0.71216	347.2103	0.00334	1E-6
Peng-Robinson	1000	300	0.71216	345.5365	0.00333	1E-6
Redlich-Kwong	1000	300	0.71216	347.2054	0.00333	1E-6
Van der Waals	1000	300	0.71216	347.0547	0.00333	1E-6
Ideal gas	1000	300	0.71216	347.2476	0.00333	1E-6
Schreiber-Pitzer	5000	300	0.71274	347.0718	0.00335	2E-7
Peng-Robinson	5000	300	0.71276	342.0295	0.00334	2E-7
Redlich-Kwong	5000	300	0.71275	348.2911	0.00334	2E-7
Van der Waals	5000	300	0.71276	349.0760	0.00334	2E-7
Ideal gas	5000	300	0.71274	347.2476	0.00333	2E-7

The Schreiber-Pitzer EoS results are compared with Peng-Robinson EoS, Redlich-Kwong EoS, Van der Waals EoS, and ideal gas EoS utilizing cubic spline curve fitting for c_p values. The enthalpy percentages of differences are given in Figure 2 to Figure 5. The enthalpy percentages of differences are increasing with increasing pressure and decreasing temperature.

The enthalpy values obtained from Schreiber-Pitzer EoS have maximum difference percentages of %-13.37 from Peng-Robinson EoS values, %-9.808 from Redlich-Kwong EoS values, %3.595 from Van der Waals EoS values and %-21.9 from ideal gas EoS respectively for investigated region. The enthalpy percentages of differences decrease when the pressures decrease or the temperatures increase.

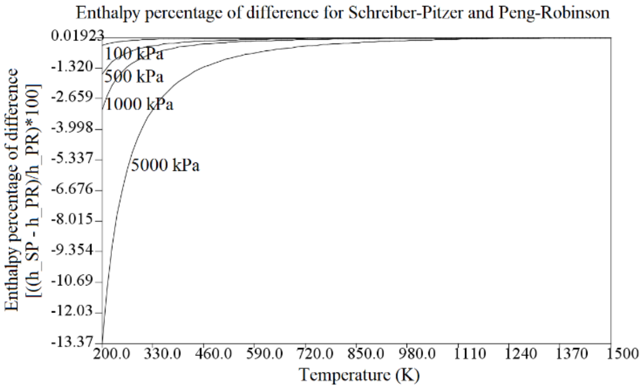

Figure 2. The enthalpy percentage of difference for Schreiber-Pitzer EoS and Peng-Robinson EoS.

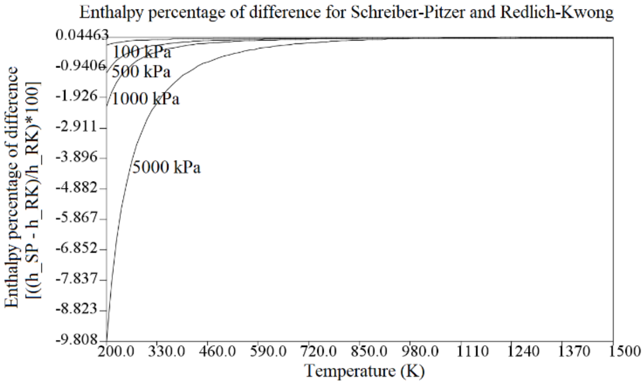

Figure 3. The enthalpy percentage of difference for Schreiber-Pitzer EoS and Redlich-Kwong EoS.

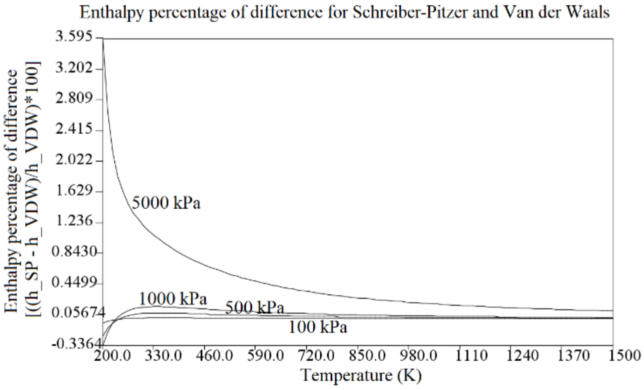

Figure 4. The enthalpy percentage of difference for Schreiber-Pitzer EoS and Van der Waals EoS.

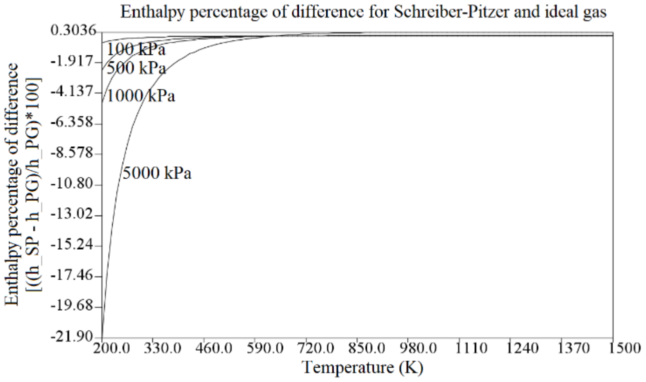

Figure 5. The enthalpy percentage of difference for Schreiber-Pitzer EoS and ideal gas EoS.

The Schreiber-Pitzer EoS entropy results are compared with Peng-Robinson EoS, Redlich-Kwong EoS, Van der Waals EoS, and ideal gas EoS results. The entropy percentages of differences are given in Figure 6 to Figure 9. The entropy percentages of differences are increasing with increasing pressure and decreasing temperature.

The entropy values obtained from Schreiber-Pitzer EoS have maximum difference percentages of %0.5828 from Peng-Robinson EoS values, %0.8808 from Redlich-Kwong EoS values, %0.6244 from Van der Waals EoS values and %1.319 from ideal gas EoS respectively for investigated region. The entropy percentages of differences decrease with increasing temperatures or decreasing pressures.

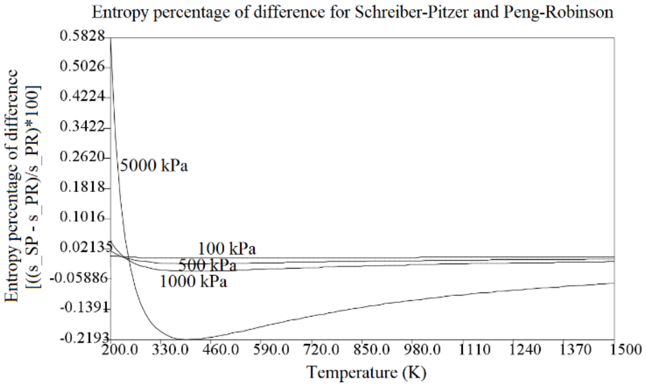

Figure 6. The entropy percentage of difference for Schreiber-Pitzer EoS and Peng-Robinson EoS.

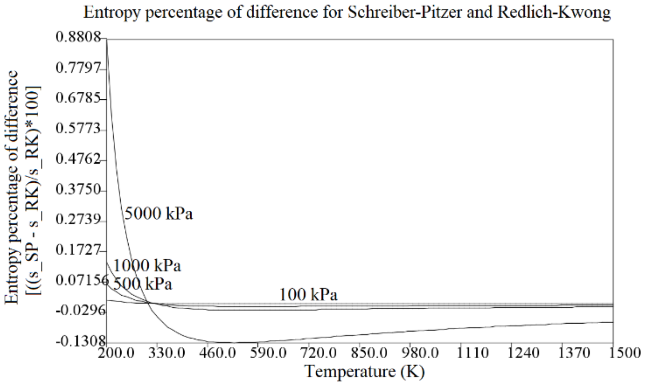

Figure 7. The entropy percentage of difference for Schreiber-Pitzer EoS and Redlich-Kwong EoS.

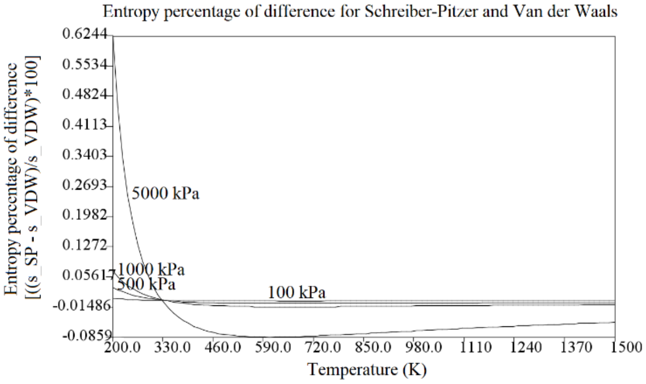

Figure 8. The entropy percentage of difference for Schreiber-Pitzer EoS and Van der Waals EoS.

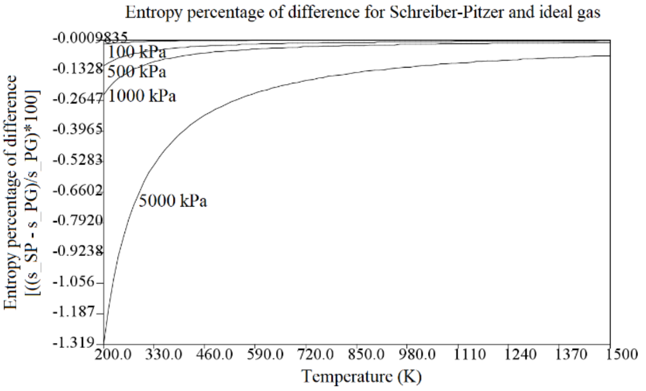

Figure 9. The entropy percentage of difference for Schreiber-Pitzer EoS and ideal gas EoS.

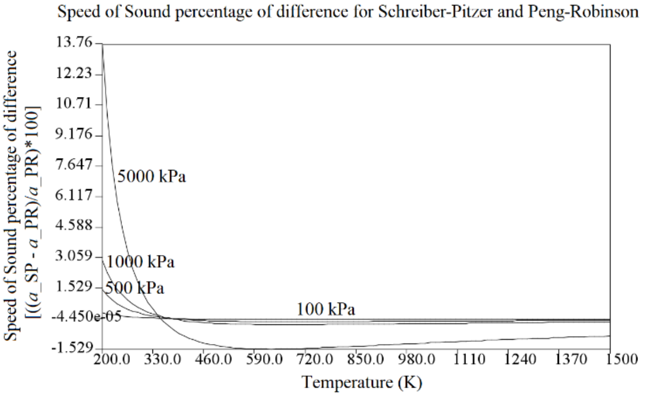

Figure 10. The speed of sound percentage of difference for Schreiber-Pitzer EoS and Peng-Robinson EoS.

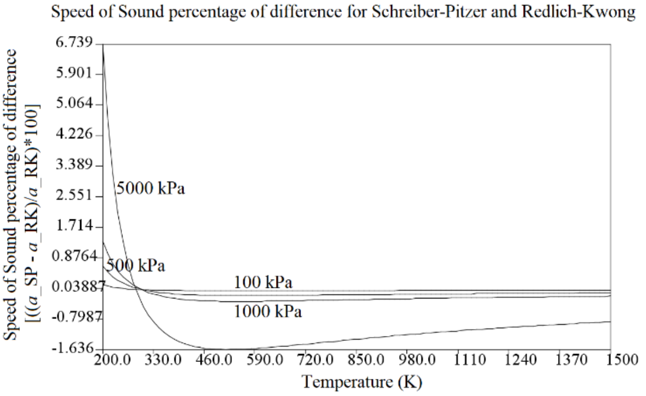

Figure 11. The speed of sound percentage of difference for Schreiber-Pitzer EoS and Redlich-Kwong EoS.

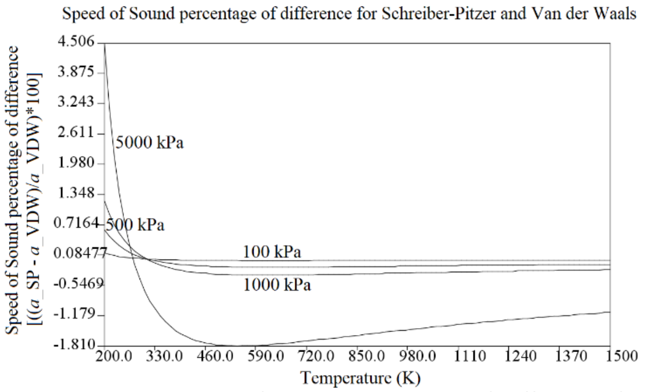

Figure 12. The speed of sound percentage of difference for Schreiber-Pitzer EoS and Van der Waals EoS.

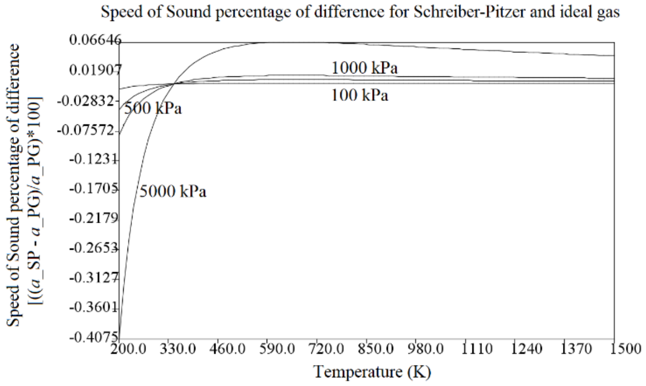

Figure 13. The speed of sound percentage of difference for Schreiber-Pitzer EoS and ideal gas EoS.

Comparisons of additional properties derived from EoS for air are investigated and the differences occurred in the speed of sound are given in Figure 10 to Figure 13. The speed of sound percentages of differences are increasing with increasing pressure and decreasing temperature.

The speed of sound values obtained from Schreiber-Pitzer EoS have maximum difference percentages of %13.76 from Peng-Robinson EoS values, %6.739 from Redlich-Kwong EoS values, %4.506 from Van der Waals EoS values and %-0.4075 from ideal gas EoS.

3. Conclusions

The ideal gas EoS is usually used in gas thermodynamic property calculations, but in applications with higher pressure zones, the error levels are increasing, so better accuracy of thermodynamic properties will be required for extreme cases. In this study, Schreiber-Pitzer EoS is considered for better accuracy of the thermodynamic properties of air mixtures.

The Java language is used to calculate the thermodynamic and thermophysical properties of air as a mixture of Nitrogen, Oxygen, and Argon. The Schreiber-Pitzer EoS results are compared with Peng-Robinson EoS, Redlich-Kwong EoS, Van der Waals EoS, and ideal gas EoS utilizing cubic spline curve fitting for c_p values. The percentages of differences for thermodynamic and thermophysical properties are calculated, and the percentages are increasing with increasing pressure and decreasing temperature. When the pressures decrease, the percentages of differences decrease rapidly. On the other hand, the percentages of differences decrease and have very small values when the temperatures increase.

The Schreiber-Pitzer EoS is the most accurate one compared to the other EoS. It should be noted that all these equations are general models. For better accuracy, equations of state are developed by using actual laboratory measurements. In the literature, there are not many studies that have been examined in this context. Coban in 2021, considered Schreiber-Pitzer EoS to calculate the thermodynamic properties of Nitrogen utilizing polynomial curve fitting for c_p values. The Schreiber-Pitzer EoS results are compared with Peng-Robinson EoS, Lee-Kesler EoS and ideal gas EoS [20]. Coban developed the stoichiometric chemical equilibrium algorithm by using Schreiber-Pitzer EoS. Equilibrium calculations are based on atomic mass balances and the minimization of Gibbs energy [21].

The Schreiber-Pitzer EoS is not known like other EoS, so it is not widely used. Even though main idea of Pitzer (Pitzer acentric factor) are heavily used in other well-known equation of states such as Peng-Robinson, Redlich-Kwong, Lee-Kesler EoS etc. The main reason for this is the simplicity of the other EoS. For example, Lee-Kesler EoS utilizes linear interpolation between two reference fluids based on Pitzer acentric factor, but Schreiber-Pitzer EoS utilizes higher degree curve fitting values utilizing 22 gases. Schreiber-Pitzer EoS can be used for compressibility factor calculations, real gas mixtures including moist gas mixtures and combustion processes due to its better accuracy compare to other known equation of states.

Nomenclature

A	Helmholtz energy (kJ/kg)
a	Speed of sound (m/s)
B,C,D,E,F,G,H,I	Schreiber-Pitzer EoS constants
c_p	Specific heat at constant pressure (kJ/kgK)
c_v	Specific heat at constant volume (kJ/kgK)
G	Gibbs energy (kJ/kg)
h	Enthalpy (kJ/kg)
k	Thermal conductivity (W/mK)
M	Molar mass (kg/kmol)
N	Mole
P	Pressure (kPa)
Pr	Prandtl number
R	Universal gas constant
s	Entropy (kJ/kgK)
T	Temperature (K)
T_c	Critical temperature (K)
T_r	Reduced pressure
u	Internal energy (kJ/kg)
v	Specific volume (m^3/kg)
w	Pitzer's acentric factor
Z	Compressibility factor
ρ	Density (kg/m^3)
β	Thermal expansion coefficient (1/K)
η	Viscosity (Pa.s)
β_T	Isothermal compressibility (1/Pa)

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