Thermodynamic and Thermophysical Properties of Dry Air by Using Cubic Peng-Robinson EoS for Gas Mixtures

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Abstract

Dry air is widely used in industrial and technological applications. Ideal gas EoS is used in dry air thermodynamic property calculations. For most applications, it might be sufficient, but when applications with higher pressure zones are considered, error level will increase. Peng-Robinson cubic Eq. of states is considered for better accuracy of the thermodynamic properties for dry air in this paper. So, the objective of this study is to suggest a more accurate EoS for thermodynamic and heat transfer analyses. Set of computer programs were developed in java language to calculate thermodynamic properties like specific volume, internal energy, enthalpy, entropy, Gibbs energy, Helmholtz energy, specific heat, thermal conductivity, and viscosity of dry air. The results are compared with the perfect gas EoS and the Eq.s developed by The International Association for the Properties of Water and Steam (IAPWS).

Keywords: Thermodynamic properties of dry air, thermophysical properties of dry air, Peng-Robison EoS, cubic EoS.

1. Introduction

Usually, perfect gas Eq. of state (EoS) is used in order to calculate thermodynamic and thermophysical properties of dry air because of its simplicity. It might be suitable for many applications; however, error level will increase if high-pressure applications are in the question. An Eq. of state with better accuracy of thermodynamic properties will be required for extreme cases. Moreover, in thermophysical property predictions, the approach is to assume such properties as only the function of temperature. But properties like viscosity and thermal conductivity heavily depend on pressure as well as temperature. Furthermore, such properties are quite a nonlinear function of pressure so that a linear interpolation type of correction of properties will not be correct.

Cubic Eq. of states are basically for the gas phase and can be accurate enough for high pressure applications as well. It is also possible to solve inverse Eq. v(T,P) avoiding of more complex iterative root finding process.

In this paper, Peng-Robinson model is used for critical properties and acentric factor for pure gases. The mixing rule proposed by Harstad et al. is used to extend the Peng-Robinson EoS to mixtures [1] and dry air (nitrogen, oxygen, argon, carbon dioxide, neon, helium, methane, krypton, hydrogen and xenon09 [2]. Peng-Robinson EoS model was suggested by Ding-Yu Peng and Donald B. Robinson in 1976 to achieve simple and accurate predictions such as the compressibility factor liquid phase [3-4]. Since 1976, it has been widely used in thermodynamic calculations in industrial and scientific studies [5].

The objective of this study is propose an accurate EoS for dry air compared to the ideal gas EoS for thermodynamic and heat transfer analyse. Set of computer programs were developed by using Peng-Robinson EoS for determining specific volume, internal energy, enthalpy, entropy, Gibbs energy, Helmholtz energy, specific heat, thermal conductivity, and viscosity of dry air. The results were compared with the perfect gas EoS and others EoSs developed by The International Association for the Properties of Water and Steam (IAPWS) [6].

2. Methodology
2.1 Formulation of Eq. of State

Peng-Robinson cubic Eq. of state was considered for dry exhaust gas mixture in this paper. Parameters of the Eq. is defined in terms of the critical properties and the acentric factor. Cubic Eq. of state has a general form of Eq. as [7]

$$P = \frac{RT}{v-b} - \frac{a}{v^2+ubv+wb^2} \tag{2.1}$$

Peng-Robinson EoS coefficients: u=2, w=-1 so that Eq. took the form:

$$P = \frac{RT}{v-b} - \frac{a}{v^2+2bv-b^2} \tag{2.2}$$

where

$$b = \frac{0.0780RT_{crit}}{P_{crit}} \tag{2.3}$$

$$a = \frac{0.45724R^2T_{crit}^2}{P_{crit}}[1 + f\omega(1 - T_r^{0.5})]^2 \tag{2.4}$$

$$f\omega = 0.37464 + 1.54226\omega - 0.269992\omega^2 \tag{2.5}$$

ω is the Pitzer's acentric factor calculated as:

$$\omega = -log_{10}P_{saturated\ vapor}(at\ T_r = 0.7) - 1 \tag{2.6}$$

The reduced vapor pressure $(P_r = P/P_{crit})$ at $T_r = T/T_{crit} = 0.7$ is necessary to obtain the values of ω. The Eq. can be written in the following form as well:

$$Z^3 - (1 + B^* - uB^*)Z^2 + (A^* + wB^{*2} - uB^* - uB^{*2})Z - A^*B^* - B^{*2} - wB^{*2} - wB^{*3} = 0 \tag{2.7}$$

where

$$A^* = \frac{aP}{R^2T^2} \tag{2.8}$$

$$B^* = \frac{bP}{RT} \quad (2.9)$$

$$Z = \frac{Pv}{RT} \quad (2.10)$$

So far Eq.s given above are for a single gas only. We will use the Peng-Robinson EoS for dry air as a mixture of oxygen, nitrogen, argon, carbon dioxide, etc.. A detail list of the component gases and their mole fractions in dry air is given in Table 1. More recently, Harstad, Miller, and Bellan [1] have presented computationally efficient forms of EoS for gas mixtures, particularly of Peng-Robinson EoS. They have also shown that it is possible to extend the Eq.s' validity beyond the range of data using departure functions. In this study, the mixing rule proposed by Harstad et al. is used to extend the PR Eq. of state to mixtures [1]. In particular, the parameters a and b can be obtained by

$$a = \sum_i \sum_j y_i y_j a_{ij} \quad (2.11)$$

$$b = \sum_i y_i b_i \quad (2.12)$$

where y is the mole fraction in the vapor phase and

$$b_{ij} = \frac{0.0780 R T_{crit\,ij}}{P_{crit\,ij}} \quad (2.13)$$

$$a_{ij} = \frac{0.45724 R^2 T_{crit\,ij}^2}{P_{crit\,ij}}\left[1 + f\omega_{ij}(1 - T_{r\,ij}^{0.5})\right]^2 \quad (2.14)$$

$$f\omega_{ij} = 0.37464 + 1.54226\omega_{ij} - 0.269992\omega_{ij}^2 \quad (2.15)$$

$$T_{r\,ij} = T/T_{crit\,ij} \quad (2.16)$$

The diagonal elements of the "critical coefficients" matrices are equal to their corresponding pure substance counterparts, i.e., $T_{crit\,ii} = T_{crit\,i}$, $P_{crit\,ii} = P_{crit\,i}$, and $\omega_{ii} = \omega_i$. The off-diagonal elements are evaluated through additional rules:

$$P_{crit\,ij} = \frac{Z_{crit\,ij} R T_{crit\,ij}}{V_{crit\,ij}} \quad (2.17)$$

$$V_{crit\,ij} = \frac{1}{8}\left[(V_{crit\,ii})^{1/3} + (V_{crit\,jj})^{1/3}\right] \quad (2.18)$$

$$Z_{crit\,ij} = \frac{1}{2}\left[Z_{crit\,ii} + Z_{crit\,jj}\right] \quad (2.19)$$

$$\omega_{ij} = \frac{1}{2}\left[\omega_{ii} + \omega_{jj}\right] \quad (2.20)$$

$$T_{crit\,ij} = \sqrt{T_{crit\,ii} T_{crit\,jj}}(1 - k_{ij}) \quad (2.21)$$

where interaction coefficient k_{ij} can be calculated as:

$$k_{ij} = 1 - \frac{(V_{crit\,ii} V_{crit\,jj})^{1/2}}{V_{crit\,ij}} \quad (2.22)$$

Partial derivatives with respect to a are

$$\frac{\partial a}{\partial T} = -\frac{1}{T}\sum_i \sum_j \left(y_i y_j a_{ij}\frac{f\omega_{ij}\sqrt{T_{r\,ij}}}{1 + f\omega_{ij}(1 - \sqrt{T_{r\,ij}})}\right) \quad (2.23)$$

$$\frac{\partial^2 a}{\partial T^2} = \frac{0.457236 R^2}{2T}\sum_i \sum_j \left(y_i y_j a_{ij}(1 - f\omega_{ij})\frac{T_{crit\,ij}}{P_{crit\,ij}}\sqrt{T_{r\,ij}}\right) \quad (2.24)$$

The basic formulas to calculate cubic roots analytically are as follows (Tartaglia & Cardano (1530)):

$$y = a_0 + a_1 x + a_2 x^2 + a_3 x^3 \quad (2.25)$$

$$a = a_2/a_3 \quad b = a_1/a_3 \quad c = a_0/a_3 \quad (2.26)$$

$$y = c + bx + ax^2 + x^3 \quad (2.27)$$

$$Q = \frac{a^2 - 3b}{9} \quad z = 2a^3 - 9ab + 27c \quad (2.28)$$

$$R = z/54 \quad (2.29)$$

$$if(R^2 < Q^3)$$

$$\begin{cases} \theta = cos^{-1}\left(\frac{R}{\sqrt{Q^3}}\right) \\ x_0 = -2\sqrt{Q}\cos[\theta/3] - a/3 \\ x_1 = 2\sqrt{Q}\cos[(\theta - 2\pi)/3] - a/3 \\ x_2 = 2\sqrt{Q}\cos[(\theta - 2\pi)/3] - a/3 \end{cases}$$

$$else\begin{cases} A = -\left(R + \sqrt{R^2 - Q^3}\right)^{1/3} \\ if(a == 0)B = 0 \\ else\ B = Q/A \\ x_0 = (A + B - a/3) \\ x_1 = \left[\left(-\frac{A+B}{2}\right) - a/3\right] + \left[\frac{\sqrt{3(A-B)}}{2}\right]i \\ x_2 = \left[\left(-\frac{A+B}{2}\right) - a/3\right] - \left[\frac{\sqrt{3(A-B)}}{2}\right]i \end{cases}$$

$$(2.30)$$

To solve the Peng-Robinson EoS for dry air as a mixture of gases, the specific heat, $C_p(T)$, for each component gas is required. This is obtained from NIST (National Institute of Standards and Technology) thermochemical tables [7]. Since $C_p(T)$ value is for the ideal gas, ideal gas mixing rule applied to establish $C_p(T)$ value of the mixture from the given gases. For each individual gas, the following partial difference curve fitting formula is used.

$$C_{pi}(T) = A_i + B_i 10^{-3}T + \frac{C_i 10^5}{T^2} + D_i 10^{-6}T^2 \quad T_{Li} \le T \le T_{Hi} \quad (2.31)$$

Component mole fractions and critical properties of dry air are given in Table 1.

Table 1. Composition and critical properties of dry air.

Name	Mol %	T_c	P_c	Z_c	ω
Nitrogen	78.084	126.2	33.9	0.29	0.039
Oxygen	20.946	154.6	50.4	0.288	0.025
Argon	0.934	150.8	48.7	0.291	0.001
Carbon dioxide	0.0397	304.1	73.8	0.274	0.239
Neon	0.001818	44.4	27.6	0.311	-0.029
Helium	0.000524	5.19	2.27	0.302	-0.365
Methane	0.000179	190.4	46	0.288	0.011
Krypton	0.000001	209.4	55	0.288	0.005
Hydrogen	0.0000005	33	12.9	0.303	-0.216
Xenon	0.00000009	289.7	58.4	0.287	0.008

The values of C_p are predicted from Eq. (2.31) and the values for nitrogen and oxygen are shown in Figures 1 and 3 respectively. The error values are given in Figures 2 and 4. The curve fitting coeffiients of argon, nitrogen and oxygen are given in Table 2, 3 and 4, respectively.

Table 2. Cp (kJ/kmol K) partial continuous curve fitting Eq. constants for Argon.

i	Ai	Bi	Ci	Di	$T_{L,i}$	$T_{H,i}$
0	20.786	0.00E+00	0.00E+00	0.00E+00	100	6000
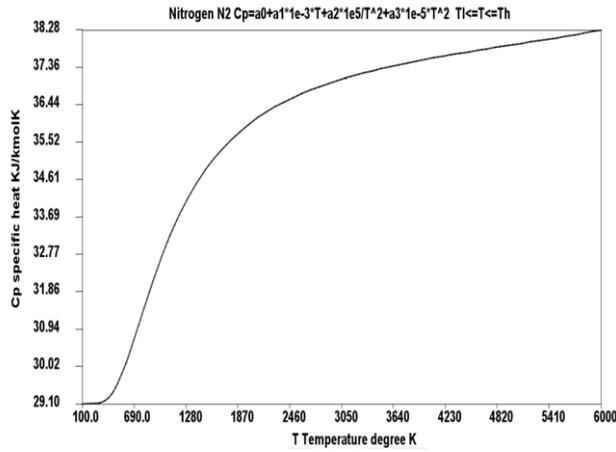
Figure 1. Change of C_P with temperature for Nitrogen kJ/(kmol K).

Figure 2. Change of error levels of predictions with temperature of C_p in Nitrogen kJ/(kmol K).

Figure 3. Change of C_P with temperature for Oxygen kJ/(kmol K).
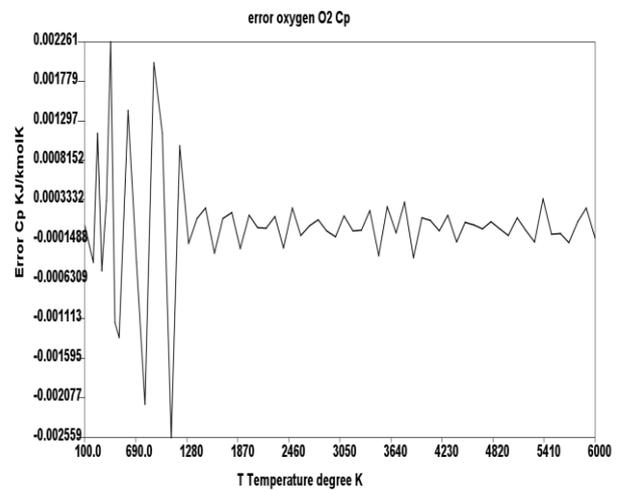
Figure 4. Change of error levels of predictions with temperature of C_p in Oxygen kJ/(kmol K).

Table 3. Cp (kJ/kmol K) curve fitting Eq. constants for Nitrogen.

i	Ai	Bi	Ci	Di	$T_{L,i}$	$T_{H,i}$
0	29.40863	-2.25144	-0.01247	4.52088	100	350
1	27.64616	0.88235	0.77007	4.76442	350	700
2	21.60170	14.87841	3.81280	-4.16546	700	1200
3	29.83076	5.42156	-15.04309	-1.08961	1200	1700
4	35.47674	0.97358	-42.54762	-0.09746	1700	2200
5	34.92820	1.31940	-38.18419	-0.15991	2200	2700
6	36.26252	0.58150	-50.89836	-0.04573	2700	3200
7	35.65734	0.76616	-34.66593	-0.05981	3200	3700
8	36.41804	0.43259	-44.18470	-0.02015	3700	4200
9	38.07768	-0.15296	-80.31180	0.03679	4200	4700
10	37.76028	-0.04994	-73.10115	0.02776	4700	5200
11	39.97385	-0.85455	-77.57593	0.10125	5200	6000

Table 4. Cp (kJ/kmol K) curve fitting Eq. constants for Oxygen.

i	Ai	Bi	Ci	Di	$T_{L,i}$	$T_{H,i}$
0	30.43604	-11.22375	-0.04709	26.32148	100	350
1	21.00131	23.61241	2.04654	-10.13517	350	700
2	29.74259	7.978910	-6.12334	-2.24031	700	1200
3	36.31276	0.050814	-19.65528	0.45704	1200	1700
4	33.34540	2.32860	-4.52664	-0.03714	1700	2200
5	31.03636	3.80481	11.95127	-0.30141	2200	2700
6	29.75055	4.50498	24.83303	-0.40859	2700	3200
7	32.14685	3.46653	-12.25985	-0.28271	3200	3700
8	43.52700	-0.66976	-268.79475	0.14080	3700	4200
9	54.76822	-4.21849	-604.90568	0.45650	4200	4700
10	63.26081	-6.72640	-894.08145	0.66490	4700	5200
11	71.31479	-8.89365	-1220.2917	0.82844	5200	6000

2.2 Formulations of Thermodynamic Properties

Now we can establish other thermodynamic properties of dry air which is not given directly by the Peng-Robinson EoS. Entropy of dry air is expressed as

$$ds = \frac{C_v(T)}{T} dT + \left(\frac{\partial P(T,v)}{\partial T}\right)_v dv \tag{2.32}$$

$$ds = \frac{R - C_p(T)}{T} dT + \left(\frac{\partial P(T,v)}{\partial T}\right)_v dv \tag{2.33}$$

$$s(T,V) = s_0 + \int_{T_0}^{T} \frac{C_p(T)-R}{T} dT + \int_{v_0}^{v} \left(\frac{\partial P}{\partial T}\right)_v dv \qquad (2.34)$$

The last term of Eq. (2.34) can be evaluated as

$$\int_{v_0}^{v} \left(\frac{\partial P}{\partial T}\right)_v dv = \int_{v_0}^{v} \left[\frac{R}{v-b} - \left(\frac{1}{v^2+2bv-b^2}\right)\left(\frac{\partial a}{\partial T}\right)_v\right] dv =$$
$$\int_{v_0}^{v} \left[\frac{R}{v-b}\right] dv - \left(\frac{\partial a}{\partial T}\right)_v \int_{v_0}^{v} \left(\frac{1}{v^2+2bv-b^2}\right) dv \qquad (2.35)$$

$$\int_{v_0}^{v} \left(\frac{1}{v^2+2bv-b^2}\right) dv = \int_{v_0}^{v} \left(\frac{1}{(v+b)^2-2b^2}\right) dv \qquad (2.36)$$

$$X = (v+b) \qquad A = \sqrt{2}b \qquad (2.37)$$

$$\int \frac{1}{X^2-A^2} dX = \int \frac{1}{(X-A)(X+A)} dX = \frac{1}{2A}\left[\int \frac{1}{X-A} dX + \int \frac{1}{X+A} dX\right] \qquad (2.38)$$

$$\int_{v_0}^{v} \left(\frac{1}{v^2+2bv-b^2}\right) dv = \frac{1}{2\sqrt{2}b}\left[ln\frac{(v+b-\sqrt{2}b)}{(v+b+\sqrt{2}b)} - ln\frac{(v_0+b-\sqrt{2}b)}{(v_0+b+\sqrt{2}b)}\right] \qquad (2.39)$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b} - \frac{\partial}{\partial a}\left(\frac{a}{v^2+2bv-b^2}\right)\left(\frac{\partial a}{\partial T}\right)_v = \frac{R}{v-b} - \left(\frac{1}{v^2+2bv-b^2}\right)\left(\frac{\partial a}{\partial T}\right)_v \qquad (2.40)$$

Internal energy of dry air can be derived similarly as

$$du = C_v(T)dT + \left(T\left(\frac{\partial P(T,v)}{\partial T}\right)_v - P(T,v)\right) dv \qquad (2.41)$$

$$du = \left(R - C_p(T)\right)dT + \left(T\left(\frac{\partial P(T,v)}{\partial T}\right)_v - P(T,v)\right) dv \qquad (2.42)$$

$$u(T,v) = u_0 + \int_{T_0}^{T}(C_p(T)-R)dT + \int_{v_0}^{v}\left(T\left(\frac{\partial P(T,v)}{\partial T}\right)_v - P(T,v)\right) dv \qquad (2.43)$$

Second integral part of the Eq. 2.43 can be evaluated as

$$\int_{v_0}^{v}\left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] = \int_{v_0}^{v}\left[\frac{RT}{v-b} - \left(\frac{1}{v^2+2bv-b^2}\right)T\left(\frac{\partial a}{\partial T}\right)_v - \left(\frac{RT}{v-b} - \frac{a}{v^2+2bv-b^2}\right)\right] dv = \int_{v_0}^{v}\left[\left[a - T\left(\frac{\partial a}{\partial T}\right)_v\right]\left(\frac{1}{v^2+2bv-b^2}\right)T\left(\frac{\partial a}{\partial T}\right)_v\right] dv \qquad (2.44)$$

$$\int_{v_0}^{v}\left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] = \frac{\left[a-T\left(\frac{\partial a}{\partial T}\right)_v\right]}{2\sqrt{2}b}\left[ln\frac{(v+b-\sqrt{2}b)}{(v+b+\sqrt{2}b)} - ln\frac{(v_0+b-\sqrt{2}b)}{(v_0+b+\sqrt{2}b)}\right] \qquad (2.45)$$

Enthalpy of dry air is expressed as

$$h(T,v) = u + vP(T,v) \qquad (2.46)$$
$$h(T,v) = h(T,v) - TP(T,v) \qquad (2.47)$$

Specific heat at constant pressure is expressed as

$$C_p(T) = \sum_{i=0}^{n-1} y_i \, C_{pi}(T) = \sum_{i=0}^{n-1} y_i\left[A_i + B_i 10^{-3}T + \frac{C_i 10^5}{T^2} + D_i 10^{-6}T^2\right] \qquad T_{L0} \leq T \leq T_{H0} \qquad (2.48)$$

Specific heat at constant volume is expressed as

$$C_v(T) = C_p(T) - R = \sum_{i=0}^{n-1} y_i \, C_{vi}(T) \qquad (2.49)$$

Where $C_{vi}(T)$ is the specific heat at constant volume of each component gases.

$$C_v(T) = \sum_{i=0}^{n-1} y_i\left(A_i - R + B_i 10^{-3}T + \frac{C_i 10^5}{T^2} + D_i 10^{-6}T^2\right) \qquad (2.50)$$

$$\int_{T_{L_0}}^{T} C_v(T)dT = \sum_{i=0}^{m-1}\left[(A_i-R)(T_{Hi}-T_{Li}) + \frac{B_i}{2}10^{-3}(T_{Hi}^2 - T_{Li}^2) - C_i 10^5\left(\frac{1}{T_{Hi}} - \frac{1}{T_{Li}}\right) + \frac{D_i 10^{-6}}{3}(T_{Hi}^3 - T_{Li}^3)\right] + \left[A_m(T - T_{Lm}) + \frac{B_m}{2}10^{-3}(T^2 - T_{Lm}^2) - C_m 10^5\left(\frac{1}{T} - \frac{1}{T_{Lm}}\right) + \frac{D_m 10^{-6}}{3}(T^3 - T_{Lm}^3)\right] \qquad (2.51)$$

for $T_0 = T_{L0} = 100\ K$ and $T_{Lm} \leq T \leq T_{Hm}$

$$\int_{T_0}^{T} C_v(T)dT = \sum_{i=0}^{n-1} y_i \int_{T_0}^{T} C_{vi}(T)dT \qquad (2.52)$$

for $T_0 = T_{L0} = 100\ K$ and $T_{Lm} \leq T \leq T_{Hm}$

$$\int_{T_0}^{T} \frac{C_v(T)dT}{T} = \sum_{i=0}^{n-1} y_i \int_{T_0}^{T} \frac{C_{vi}(T)dT}{T} \qquad (2.53)$$

To adopt Eqs. (2.52) and (2.53) to any other reference point T_r

$$\int_{T_r}^{T} C_{vi}(T)dT = \int_{T_0}^{T} C_{vi}(T)dT - \int_{T_0}^{T_r} C_{vi}(T)dT \qquad (2.54a)$$

$$\int_{T_r}^{T} \frac{C_{vi}(T)}{T} dT = \int_{T_0}^{T} \frac{C_{vi}(T)}{T} dT - \int_{T_0}^{T_r} \frac{C_{vi}(T)}{T} dT \qquad (2.54b)$$

2.4 Formulations of Thermophysical Properties

To estimate the thermal conductivity and viscosity of dry air, equations suggested by Kadoya et al [8] are used.

$$\eta(T_r, \rho_r) = H\left[\eta_0(T_r) + \Delta\eta(\rho_r)\right] \qquad (2.55)$$

where

$$\eta_0(T_r) = A_0 T_r + A_1 T_r^{0.5} + A_2 + \frac{A_3}{T_r} + \frac{A_4}{T_r^2} + \frac{A_5}{T_r^3} + \frac{A_6}{T_r^4} \qquad (2.56)$$

As it can be seen in Eq. (2.56), the η_0(low pressure viscosity) depends on only temperature, and the $\Delta\eta$ is the difference between low and high pressure viscosity

$$\Delta\eta(\rho_r) = \sum_{i=1}^{4} B_i \rho_r^i \qquad (2.57)$$

There is a similar approach for thermal conductivity.

$$k(T_r, \rho_r) = \Lambda\left[k_0(T_r) + \Delta k(\rho_r)\right] \qquad (2.58)$$

where

$$k_0(T_r) = C_0 T_r + C_1 T_r^{0.5} + C_2 + \frac{C_3}{T_r} + \frac{C_4}{T_r^2} + \frac{C_5}{T_r^3} + \frac{C}{T_r^4} \qquad (2.59)$$

$$\Delta k(\rho_r) = \sum_{i=1}^{4} D_i \rho_r^i \qquad (2.60)$$

$$\rho_r = \rho/\rho^* \qquad T_r = T/T^* \qquad (2.61)$$

In Eqs. (2.55) to (2.60), ρ^* is equal to 314.3 kg/m^3, Λ is equal to 25.9778 $(10^{-3}W/(mK)$, H is equal to 6.1609 (10-6 Pas) and T^* is equal to 132.5 K. The coefficients of Eqs. (2.55) to (2.60) are given in Table 5.

Table 5. Coefficients of Eqs.(2.55) to (2.60). [8]

i	A_i	B_i	C_i	D_i
0	0.128517	0.465601	0.239503	0.402287
1	2.60661	1.26469	0.006497	0.356603
2	-1	-0.511425	1	-0.163159
3	-0.709661	0.2746	-1.92615	0.138059
4	0.662534		2.00383	-0.020172
5	-0.197846		-1.07553	
6	0.0077014		0.229414	

Table 6. Additional properties derived from Peng-Robinson EoS

Properties	Formula
Speed of sound[10]	$v_s = \sqrt{-\left(\dfrac{v^2 C_p}{C_v M}\right)\left(\dfrac{\partial P}{\partial v}\right)_T}$ $= \sqrt{\left(\dfrac{v^2 C_p}{C_v M}\right)\left(\dfrac{RT}{(v-b)^2} - \dfrac{2a(v+b)}{(v^2 + 2bv - b^2)}\right)}$
Thermal expansion coefficient	$\beta = -\dfrac{1}{\rho}\left(\dfrac{\partial \rho}{\partial T}\right)_P$
Isothermal compressibility	$\beta_T = \sqrt{\dfrac{v}{\left(\dfrac{\partial P}{\partial v}\right)_T}}$ $= \sqrt{\dfrac{v}{\left(\dfrac{RT}{(v-b)^2} - \dfrac{2a(v+b)}{(v^2 + 2bv - b^2)^2}\right)}}$

3. Results

Several programs were developed in java language to carry out the predictions. The names of programs are given in Table 6. Air_IAPWS was developed by using IAPWS formulations [6] and air_PG is for the perfect gas EoS for air. The details of these programs are not described here, but they are given for comparison purposes.

Table 6. Programs developed for calculating dry air properties.

Model Name	Reference and Description
air_IAPWS	IAPWS Formulation [6]
air_PR	Peng-Robinson EoS for mixtures [11]
air_PG	Perfect gas EoS as a single gas.

Figure 5. Peng-Robinson EoS *program graphic output for P=100 kPa and T=300 K.*

Results obtained for several thermodynamic properties by using different EoSs are compared in Table 7.

Table 7. Comparisons of the three different EoS for dry air.

Model	P (kPa)	T (deg. K)	v (m³/kg)	h (kJ/kg)	u (kJ/kg)	s (kJ/(kg.K))
air_PR	100	300	0.86068	27.49786	19.76670	0.09428
air_PG	100	300	0.86114	27.01007	19.30280	0.09809
air_IAPWS	100	300	0.86088	27.01361	19.28572	0.09810
air_PR	500	300	0.17178	26.32825	18.77558	-0.36967
air_PG	500	300	0.17222	27.01007	19.30280	-0.36388
air_IAPWS	500	300	0.17197	26.11119	18.48476	-0.36653
air_PR	1000	300	0.08568	24.88375	17.54150	-0.57105
air_PG	1000	300	0.08611	27.01007	19.30280	-0.56285
air_IAPWS	1000	300	0.08587	24.99335	17.48330	-0.56881
air_PR	3000	300	0.02832	19.30848	12.66731	-0.89554
air_PG	3000	300	0.02870	27.01007	19.30280	-0.87821
air_IAPWS	3000	300	0.02850	20.62849	13.47535	-0.89723
air_PR	100	500	1.43560	230.79834	165.57513	0.61237
air_PG	100	500	1.43524	230.10497	164.98788	0.61632
air_IAPWS	100	500	1.43571	230.10855	164.89739	0.61633
air_PR	500	500	0.28741	230.17163	164.80265	0.15019
air_PG	500	500	0.28704	230.10497	164.98788	0.15434
air_IAPWS	500	500	0.28752	229.90383	164.50290	0.15356
air_PR	1000	500	0.14389	229.39896	163.84406	-0.04900
air_PG	1000	500	0.14352	230.10497	164.98788	-0.04462
air_IAPWS	1000	500	0.14400	229.65482	164.01187	-0.04637
air_PR	3000	500	0.04822	226.42496	160.08668	-0.36516
air_PG	3000	500	0.04784	230.10497	164.98788	-0.35998
air_IAPWS	3000	500	0.04834	228.73108	162.07077	-0.36553

In the following figures, the Peng-Robinson EoS is compared with the perfect gas EoS and IAPWS for the dry air EoS. IAPWS equation is based on the experimental data. The results of Peng-Robinson EoS are falling between the results of perfect gas EoS and IAPWS. This is the expected behavior for such a general EoS based on acentric factor.
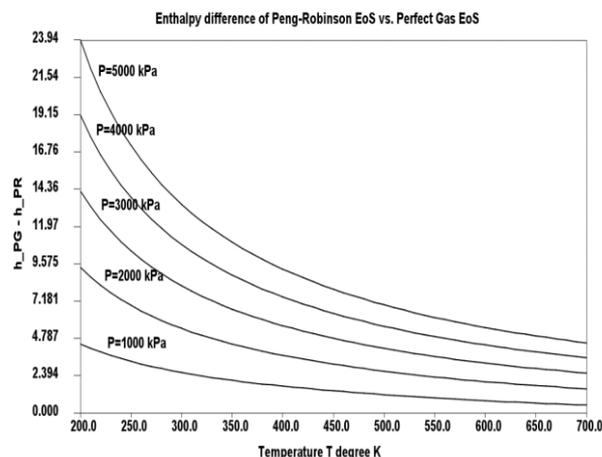
Figure 6. Enthalpy difference of Peng-Robinson and perfect gas EoS (for above 1000 kPa).
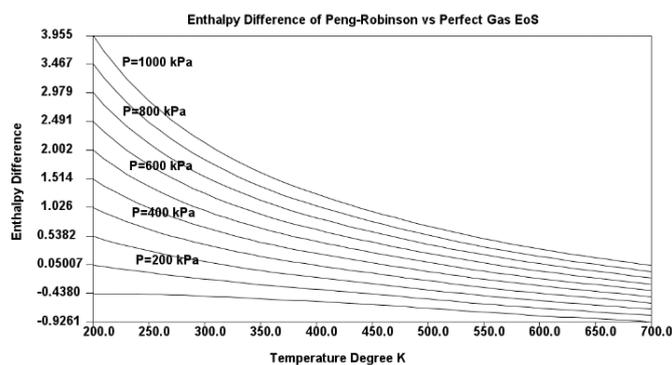
Figure 7. Enthalpy differences of Peng-Robinson and perfect gas EoS.
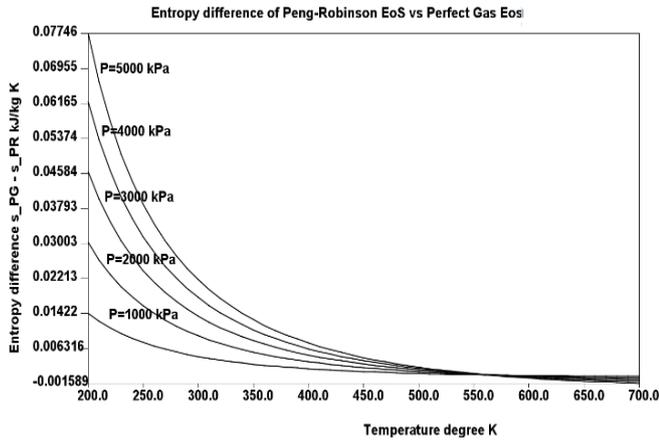
Figure 8. Entropy difference of Peng-Robinson and perfect gas EoS.

Figure 9. Speed of sound difference of Peng-Robinson and perfect gas EoS.
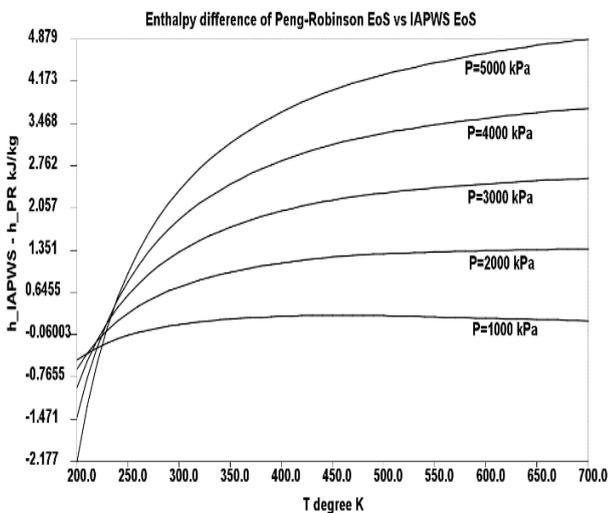
Figure 10. Enthalpy difference of Peng-Robinson and IAPWS EoS.

Figure 11. Entropy difference of Peng-Robinson and IAPWS EoS.

4. Conclusions

There are accurate EoS already available for air as a real gas. However, this package can be utilized as a calibration tool for a gas mixture to be used in combustion processes. Another basic application of such an EoS is to use it as a base to define humid air, which will be carried out by the authors in a separate publication.

Computer models for different set of real gas EoS by IAPWS and perfect gas formulations are also derived and results are compared. The results from the Peng-Robinson equation are between the results of perfect gas EoS and IAPWS. This is the expected for such a general EoS based on the acentric factor.

All the coefficients of EoSs for property estimations of dry air are given with details, which can be used for computational purposes. Whole set of computer codes developed in java programming language for researchers are available at: www.turhancoban.com.

Nomenclature

a	Cubic Eq. coefficient (Pa kmol/m^3)
b	Cubic Eq. coefficient (m^3/kmol)
C_p	Specific heat capacity at constant pressure (J/kg K)
C_{pi}	Individual gas specific heat capacity at constant pressure (J/kg K)
C_v	Specific heat capacity at constant volume (J/kg K)
C_{vi}	Individual gas specific heat capacity at constant volume (J/kg K)
F_w	A function of w specific for Peng-Robinson EoS
h	Enthalpy (kJ/kg)
k	Thermal conductivity (W/m K)
M	Molecular weight (kg/kmol)
P	Pressure (kPa)
R	Universal gas constant (8.314 J/mol K)
s	Entropy (kJ/kg K)
T	Temperature (K)
T*	132,5 K
u	Internal energy (kJ/kg)
v	Specific volume (m^3/kg)
V	Volume (m^3)
Z	Compressibility factor

Greek symbols

β	Thermal expansion coefficient (1/k)
$β_T$	Isothermal compressibility
η	Viscosity (Pa s)

ω	Pitzer's acentric factor
Δη	Viscosity increase (Pa s)
Δk	Thermal conductivity increase (W/m K)
ρ	Density (kg/m^3)
ρ *	314.3 (kg/m^3)
v_s	Speed of sound (m/s)
υ	Molar volume (m^3/kmol)

Subscripts

crit   critical value
r   reduced value

References

[1] K.G. Harstad, R.S. Miller and J. Bellan, "efficient high-pressure state equation of states," *AICHE Journal*, Vol. 43, No. 6, pp. 1605-1610, 1997.

[2] E. W. Lemmon, R. T. Javobsen, "Viscosity and thermal conductivity eq.s for nitrogen, oxygen, argon, and air," *International Journal of Thermophysics*, Vol. 25, No. 1, January 2004.

[3] D. Peng and D. B. Robinson, "A new two-constant equation of state," *Ind. Eng. Chem., Fundam.*, Vol. 15, No. 1, 1976.

[4] Z. Nasri, B. Housam "Applications of The Peng-Robinson equation of state using MATLAB," *Chemical Engineering Education,* 43, 2009.

[5] J.S. Lopez-Echeverry, S. Reif-Acherman, E. Araujo-Lopez "Peng-Robinson equation of state: 40 years through cubics," *Fluid Phase Equilibria*, 447, 39-71, 2017.

[6] The International Association for the Properties of Water and Steam, Guideline on an Eq. of State for Humid Air in Contact with Seawater and Ice, Consistent with the IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater, Niagara Falls, Canada, IAPWS G8-10, 2010.

[7] R. C. Reid, J. M. Prausnitz, B. E. Poling, *The Properties of Gases & Liquids,* Fourth Edition, McGraw-Hill, 1987.

[8] K. Kadoya, N. Matsunaga, and A. Nagashima, "Viscosity and thermal conductivity of dry air in the gaseous phase," *Journal Physical Chemical Reference Data*, 14, 947, 1985.

[9] NIST-JANAF Thermochemical Tables [Online]. Available: https://janaf.nist.gov/, (accessed May. 1, 2020).

[10] M. Salimi, A. Bahramian, "The Prediction of the Speed of Sound in Hydrocarbon Liquids and Gases: The Peng-Robinson Eq. of State Versus SAFT-BACK", *Petroleum Science Technology,* doi: 10.1080/10916466.2011.58030132:409-417, 2014.

[11] I. H. Bell, J. Wronski, S. Quailin, and V. Lemort, "Pure and pseudo-pure fluid thermophysical property evaluation and the open-source thermophysical property library CoolProp," *Industrial & Engineering Chemistry Research,* doi: 10.1021/ie4033999, 2014.