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THERMODYNAMIC AND THERMOPHYSICAL PROPERTIES OF PURE GASES BY USING SCHEREIBER-PITZER EOS

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Abstract:In gas thermodynamic property calculations, it is usually ideal gas EoS is used. The basic reason for this is simplicity of using ideal gas EoS. For most applications it might be sufficient, but when applications with higher pressure zones are considered error level will increase. An equation of state with better accuracy of thermodynamic properties will be required for extreme cases. In this study Scheiber-Pitzer equation of state is used to establish computer programs in java language to calculate properties of gases. Scheiber-Pitzer equation of state is a general real gas EoS form that utilized Pitzer's acentricity factor and a modified Benedict Webb-Rubin EoS. It is basically quadratic curve fitting equation to reference fluids by using Pitzer's acentricity factor as variable. A rich list of curve fitting reference fluids, including hydrocarbons and other gases, are used to obtain curve fitting coefficients. Specific heat values are also needed. This values are added into the program as partial continious or polynomial curve fitting equations. All the codes are developed in java programming language and offered to third party users in <u>www.turhancoban.com</u> internet site. **Keywords:** Scheiber-PitzerEoS, thermodynamic properties of pure gases

1. Formulation of Equation of State

In this paper, We will consider Scheiber-Pitzerequation of states for pure gases. Details of the Scheiber-PitzerEoS is given below.

$$\begin{split} Z &= \frac{1}{\rho RT} = 1 + B(T_r, \rho_r)\rho_r + C(T_r, \rho_r)\rho_r^2 + D(T_r, \rho_r)\rho_r^3 \\ &+ E(T_r, \rho_r)\rho_r^5 + F(T_r, \rho_r)\rho_r^7 + G(T_r, \rho_r)\rho_r^8 \\ &+ H(T_r, \rho_r)\rho_r^{10} + I(T_r, \rho_r)\rho_r^{12} \\ B(T_r, \rho_r) &= c_1 + \frac{c_2}{T_r} + \frac{c_3}{T_r^2} + \frac{c_4}{T_r^6} \\ C(T_r, \rho_r) &= c_5 + \frac{c_6}{T_r} + \frac{c_7}{T_r^3} + \frac{c_8}{T_r^4} \exp(-\rho_r^2) = C_1(T_r) + C_2(T_r) \exp(-\rho_r^2) \\ D(T_r, \rho_r) &= c_9 + \frac{c_{10}}{T_r} + \frac{c_{11}}{T_r^2} \\ E(T_r, \rho_r) &= \frac{c_{12}}{T_r^2} + \frac{c_{13}}{T_r^3} \\ F(T_r, \rho_r) &= \frac{c_{14}}{T_r^3} + \frac{c_{15}}{T_r^3} \\ G(T_r, \rho_r) &= \frac{c_{16}}{T_r^3} + \left(\frac{c_{17}}{T_r^3} + \frac{c_{18}}{T_r^4}\right) \exp(-\rho_r^2) = G_1(T_r) + G_2(T_r) \exp(-\rho_r^2) \\ H(T_r, \rho_r) &= \left(\frac{c_{19}}{T_r^3} + \frac{c_{20}}{T_r^4}\right) \exp(-\rho_r^2) = H_2(T_r) \exp(-\rho_r^2) \end{split}$$

$$I(T_r, \rho_r) = \left(\frac{C_{21}}{T_r^3} + \frac{C_{22}}{T_r^4}\right) \exp(-\rho_r^2) = I_2(T_r) \exp(-\rho_r^2)$$

$$c_i = C_{i,0} + C_{i,1}\omega + C_{i,2}\omega^2$$

Where ω in Scheiber-Pitzer equation of states coefficient is called **Pitzer'saccentric factor**. This factor is calculated as $\omega = -log_{10}P_{saturated vapor}(at T_r = 0.7) - 1$

Table 2.1 C[i][j] Coefficients of Scheiber-PitzerEoS

	j=1	j=2	j=3
C1,j	0.4422590000	0.7256500000	0.0000000000
C2,j	-0.9809700000	0.2187140000	0.0000000000
C3,j	-0.6111420000	-1.2497600000	0.0000000000
C4,j	-0.0051562400	-0.1891870000	0.0000000000
C5,j	0.1513654000	2.3067060000	- 10.4117400000
C6,j	-0.0438262500	4.6960680000	15.1414600000
C7,j	1.1026990000	3.1293840000	-9.5214090000
C8,j	-0.6361056000	0.3266766000	2.9046220000
C9,j	0.0087596260	-3.2040990000	8.0023380000
C10,j	0.3412103000	8.8721690000	- 14.4038600000
C11,j	-0.8842722000	-6.6874710000	11.7685400000
C12,j	0.1375109000	0.2432806000	-0.5515101000
C13,j	-0.1443457000	1.2869320000	-2.1809880000
C14,j	-0.0059695540	0.0454196100	0.0000000000
C15,j	0.0245053700	-0.4158241000	0.7914067000
C16,j	-0.0041995900	0.0910596000	-0.1786378000
C17,j	0.0004665477	-1.2620280000	-2.8267720000
C18,j	-0.0194510100	0.7812220000	4.1900460000
C19,j	0.0408364300	1.3988440000	0.0000000000
C20,j	-0.0354691700	-1.4560410000	0.0000000000
C21,j	-0.0028779550	0.2104505000	0.0000000000

C22	0.0058962650	0.2191255000	0.0000000000

Derivatives of the equations:

$$\frac{\frac{\partial B(T_r, \rho_r)}{\partial T} = \frac{1}{T_c} \left[-\frac{c_2}{T_r^2} - 2\frac{c_3}{T_r^3} - 6\frac{c_4}{T_r^7} \right]}{\frac{\partial C(T_r, \rho_r)}{\partial T} = \frac{1}{T_c} \left[-\frac{c_5}{T_r^2} - 3\frac{c_7}{T_r^4} - 4\frac{c_8}{T_r^5} \exp(-\rho_r^2) \right]}{\frac{\frac{\partial D(T_r, \rho_r)}{\partial T}}{\frac{\partial T}{T}} = \frac{1}{T_c} \left[-\frac{c_{10}}{T_r^2} - 3\frac{c_{11}}{T_r^4} \right]}{\frac{\frac{\partial E(T_r, \rho_r)}{\partial T}}{\frac{\partial T}{T}} = \frac{1}{T_c} \left[-\frac{c_{12}}{T_r^2} - 3\frac{c_{13}}{T_r^4} \right]}$$

$$\begin{split} \frac{\partial F(T_r,\rho_r)}{\partial T} &= \frac{1}{T_c} \left[-2\frac{c_{14}}{T_r^3} - 3\frac{c_{13}}{T_r^4} \right] \\ \frac{\partial G(T_r,\rho_r)}{\partial T} &= \frac{1}{T_c} \left[-3\frac{c_{16}}{T_r^4} + \left(-3\frac{c_{17}}{T_r^4} - 4\frac{c_{18}}{T_r^5} \right) \exp(-\rho_r^2) \right] \\ \frac{\partial H(T_r,\rho_r)}{\partial T} &= \frac{1}{T_c} \left[\left(-3\frac{c_{19}}{T_r^4} - 4\frac{c_{18}}{T_r^5} \right) \exp(-\rho_r^2) \right] \\ \frac{\partial I(T_r,\rho_r)}{\partial T} &= \frac{1}{T_c} \left[\left(-3\frac{c_{21}}{T_r^4} - 4\frac{c_{22}}{T_r^5} \right) \exp(-\rho_r^2) \right] \end{split}$$

Helmholtz energy equation will be used to predict other thermodynamic properties

$$dA = -SdT - Pdv$$
$$\frac{\partial A}{\partial v}\Big|_{T} = -P$$
$$dA = -Pdv = \frac{P}{\rho^{2}}d\rho$$
$$A - A_{0} = \int_{\rho_{0}}^{\rho} \frac{P}{\rho^{2}}d\rho = \int_{0}^{\rho} \frac{P}{\rho^{2}}d\rho + \int_{\rho_{0}}^{0} \frac{P}{\rho^{2}}d\rho = \int_{0}^{\rho} \frac{P}{\rho^{2}}d\rho + \int_{\rho_{0}}^{0} \frac{\rho RT}{\rho^{2}}d\rho$$

The second term (limits between low density ρ_0 and density 0) can be defined as an ideal state case where $P = \rho RT$. Now we can add and substract ideal gas density term of the equation

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

Considering for real EoS $P = Z\rho RT$ equation becomes

$$A - A_{0} = \int_{\rho_{0}} \frac{P}{\rho^{2}} RT[B(T_{r},\rho_{r})\rho_{r} + C(T_{r},\rho_{r})\rho_{r}^{2} + D(T_{r},\rho_{r})\rho_{r}^{3} + E(T_{r},\rho_{r})\rho_{r}^{5} + F(T_{r},\rho_{r})\rho_{r}^{7} + G(T_{r},\rho_{r})\rho_{r}^{8} + H(T_{r},\rho_{r})\rho_{r}^{10} + I(T_{r},\rho_{r})\rho_{r}^{12}]d\rho = \int_{0}^{\rho} \frac{P}{\rho^{2}}d\rho + \int_{\rho_{0}}^{0} \frac{\rho RT}{\rho^{2}}d\rho + \int_{0}^{\rho} \frac{\rho RT}{\rho^{2}}d\rho - \int_{0}^{\rho} \frac{\rho RT}{\rho^{2}}d\rho$$

$$\begin{split} A - A_0 &= \int_0^{\rho} \frac{Z\rho RT - \rho RT}{\rho^2} d\rho + \int_{\rho_0}^{\rho} \frac{\rho RT}{\rho^2} d\rho \\ A - A_0 &= \int_0^{\rho} \frac{RT(Z-1)}{\rho} d\rho + \int_{\rho_0}^{\rho} \frac{\rho RT}{\rho^2} d\rho \\ A - A_0 &= \int_0^{\rho_r} \frac{1}{\rho_r} d\rho_r + \int_{\rho_{r0}}^{\rho_r} \frac{RT}{\rho_r} d\rho_r \\ A - A_0 &= RT \int_0^{\rho_r} [B(T_r, \rho_r) + C(T_r, \rho_r)\rho_r + D(T_r, \rho_r)\rho_r^2 + E(T_r, \rho_r)\rho_r^4 \\ &+ F(T_r, \rho_r)\rho_r^6 + G(T_r, \rho_r)\rho_r^7 + H(T_r, \rho_r)\rho_r^9 \\ &+ I(T_r, \rho_r)\rho_r^{-1}] d\rho_r + RT ln \frac{\rho_r}{\rho_{r0}} \end{split}$$

Some of the terms in this integration includes terms of exponential and power multiplications. This integrations are carried out as follows:

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

Handling these terms such as above Taylor series are much easier than taken numerical integration, then Helmholtz departure function becomes:

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

Entropy departure function:

$$\begin{split} S - S_0 &= -\frac{\partial (A - A_0)}{\partial T} \bigg|_{\rho} \\ S - S_0 &= R \left(B\rho_r + C_1 \frac{\rho_r^2}{2} + C_2 K(1,\rho_r) + D \frac{\rho_r^3}{3} + E \frac{\rho_r^5}{5} + F \frac{\rho_r^8}{8} + G_1 \frac{\rho_r^9}{9} \\ &+ G_2, K(8,\rho_r) + H_2 K(10,\rho_r) + I_2 K(12,\rho_r) \right) \\ &+ RT \left(\frac{dB}{dT} \rho_r + \frac{dC_1}{dT} \frac{\rho_r^2}{2} + \frac{dC_2}{dT} K(1,\rho_r) + \frac{dD}{dT} \frac{\rho_r^3}{3} \\ &+ \frac{dE}{dT} \frac{\rho_r^5}{5} + \frac{dF}{dT} \frac{\rho_r^8}{8} + \frac{dG_1}{dT} \frac{\rho_r^9}{9} + \frac{dG_2}{dT} K(8,\rho_r) \\ &+ \frac{dH_2}{dT} K(10,\rho_r) + \frac{dI_2}{dT} K(12,\rho_r) \right) + Rln \left(\frac{\rho_r}{\rho_{r0}} \right) \end{split}$$

Enthalpy departure function:

 $H - H_0 = (A - A_0) + T(S - S_0) + RT(Z - 1)$ Internal energy departure function:

$$U - U_0 = (A - A_0) + T(S - S_0)$$

Gibbs energy departure function: $G - G_0 = (A - A_0) + RT(Z - 1)$

$$G - G_0 = (A - A_0) + RI(Z - 1)$$

The fugacity-pressure ratio: $f (A - A_0)$

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

Data is also needed to solve $C_p(T)$ value. In order to NIST tables establish that, given at the adresshttps://janaf.nist.gov/ is used. The following partial continuous formulation is taken. the following partial difference curve fitting formula is used

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

As an example case of Partial continuous curve fitting of Cp values Data for Nitrogen is given below.



Figure 2.1 Cp of Nitrogen kJ/(kmolK)



Figure 2.2 Error of Cp in Nitrogen kJ/(kmolK) Table 2.2 Cp (kJ/kmol K) partial continious curve fitting equations for N₂ Nitrogen

1	mone for f	2 1 111 0 801				U and D
i	Ai	Bi	Ci	Di	T _{li} K	Π_2 and D_2
0	29.4086307829	-2.2514470327	-0.0124732186	4.5208886188	100	$F_{\tilde{Q}} = 1.220_{350}^{-1} \{1 + 0.0038\}$
1	27.6461690069	0.8823555268	0.7700742081	4.7644228675	350	Where $Q=1.3\%$ (He), $Q=0.3\%$
2	21.6017064500	14.8784143146	3.8128084889	- 4.1654669506	700	1200
3	29.8307659455	5.4215607907	-15.0430960215	- 1.0896138268	1200	If the gas pressure is high
4	35.4767415122	0.9735825946	-42.5476274875	- 0.0974664401	1700	not be valid anymore and 2200
5	34.9282028043	1.3194039653	-38.1841919451	- 0.1599114820	2200	should be taken into the a 2700 described high pressure
6	36.2625256395	0.5815001033	-50.8983620805	- 0.0457311313	2700	following equations
7	35.6573409828	0.7661686027	-34.6659363416	- 0.0598170521	3200	$Z_1 = \eta^0 \xi = [0.80^{77} T_r^{0.618} - 0.357$
8	36.4180454205	0.4325957723	-44.1847062013	- 0.0201521727	3700	4200 + 0.018]
9	38.0776880528	-0.1529603974	-80.3118075101	0.0367938172	4200	Where η ⁰ refrees the low pr
10	37.7602843891	-0.0499492999	-73.1011559910	0.0277685442	4700	If $T \leq 1$ and $P \leq \left(\frac{P_{vp}}{P}\right)$
11	39.9738552178	-0.8545553355	-77.5759376892	0.1012534665	5200	$\frac{1}{6000} \frac{1}{P_c}$

For some gases only data is available is in polynomial curve fitting format, for this cases polynomial form is assumed.

2. Formulations of other thermophysical and thermodynamic properties

In order to calculate thermopysical properties (thermal conductivity and viscosity) of dry two approaches taken. If data is available (usually available only for low pressure gases) a curve fitting of high degree polynomial is applied, such as:

$$\eta_0(T) = \sum_{n=0}^{N} a_n T^n \quad (3.1)$$
$$k_0(T) = \sum_{n=0}^{N} b_n T^n \quad (3.2)$$

i

If data is not available Lucas approach is used for low pressure viscosity. Lucas[21],[22],[23],[5] suggested the following correlations:

$$\eta \xi = f(T_r) = [0.807T_r^{0.618} - 0.357 \exp(-0.449T_r) + 0.340 \exp(-4.058T_r) + 0.018]F_p^0 F_Q^0 (3.3)$$

Where
$$\xi = 0.01 \left[\frac{(RT_c)(N_0)^2}{M^3 P_c^4} \right]^{1/6}$$
 where

R=8314.46261815324 J/(kmolK) is universal gas constant N₀=6.02214076x10²⁶ 1/(kmol) is Avagadro's constant. Pc is the critical pressure in kPa, Tc is the critical temperature in degree K, M is molecular weight in kg/kmol, $T_r = \frac{T}{T_r}$ is reduced temperature.

 μ_r is dimensionless dipole moment and μ is dipole moment in debyes. Lucas et al defined μ_r as

$$\mu_r = 0.5246 \frac{\mu^2 P_c}{T_c}$$

Correction factor F_p^0 defined as:

 $F_{p}^{0} = 1$ $0 \le \mu_r < 0.022$ $F_p^0 = 1 + 30.55(0.292 - Z_c)^{1.72}$ $0.022 \le \mu_r < 0.075$ $F_p^0 = 1 + 30.55(0.292 - Z_c)^{1.72}[0.96 + 0.1(T_r - 0.7)]$ $0.075 \le \mu_r$ Correction factor F_n^0 is used only for the quantum gases He,

$$\frac{12 \text{ and } D_2}{F_Q^0 = 1.22} \frac{\text{Taik} K}{350} \{1 \pm 0.00385! (T_r - 12)^2\}^{1/M} sign(T_r - 12)\}$$
Where Q=1 38(He), Q=0.76(H₂), Q=0.52(D₂)
1200
f the gas pressure is high, low pressure estimations will
not be valid anymore and effect of pressure in viscosity
hould be taken into the account. Lucas[124],[125][126]
lescribed ligh pressure gas viscosity by using the
ollowing equations
 $Z_1 = n^0 \xi = [0.8077_r^{0.618} - 0.357 \text{ exp}(-0.449T_r) 0.34 \text{ exp}(-4.058T_r) + 4200 + 0.018]F_p^0 F_Q^0$ (3.8)
Where n^0 refress the low pressure viscosity.
 $f = T_r \le 1 \text{ and } \frac{220}{T_r} < \frac{P_{vp}}{P_c} + (6.99P^\beta - 0.6)(1 - T_r)$

$$Z_{2} = 0.6 + 0.76P_{r}^{\alpha} + (6.99P_{r}^{\beta} - 0.6)(1 - T_{r})$$

With $\alpha = 3.262 + 14.98P_{r}^{5.508}$
 $\beta = 1.390 + 5.746P_{r}$

If $1 \le T_r \le 1$ and $0 \le P_r \le 100$ then

$$Z_2 = Z_1 \left[1 + \frac{aP_r^e}{b + P_r^f + (1 + cP_r^d)^{-1}} \right]$$
$$a = \frac{a_1}{T_r} \exp(\alpha_2 T_r^a) \quad b = a(\beta_1 T_r - \beta_2)$$
$$c = \frac{c_1}{T_r} \exp(c_2 T_r^c) \quad d = \frac{d_1}{T_r} \exp(d_2 T_r^e)$$
$$e=1.3088$$
$$f=f_1 \exp(f_1 T_r^{\xi})$$

Table 3.10 Coefficients of eqn (3.10)

	- · · · ·	
$a_1 = 1.245 \times 10^{-3}$	$a_2 = 5.1726$	$\gamma = -0.3286$
$b_1 = 1.6553$	$b_2 = 1.2723$	
$c_1 = 0.4489$	$c_2 = 3.0578$	$\delta = -37.7332$
$d_1 = 1.7368$	$d_2 = 2.2310$	$\epsilon = -7.6351$
$f_1 = 0.9425$	$f_2 = -0.1853$	

After computing Z_1 and Z_2 calculate correction factors F_P and F_Q as:

$$Y = \frac{Z_2}{Z_1} (3.11)$$

$$F_p = \frac{1 + (F_p^0 - 1)Y^{-3}}{F_p^0} (3.12)$$

$$F_q = \frac{1 + (F_q^0 - 1)[Y^{-1} - 0.007(\ln(Y))^4]}{F_q^0} (3.13)$$

 F_p^0 and F_Q^0 are low pressure polarity and quantum factors.

Low pressure polarity F_p^0 defined as: $F_p^0 = 1$ $0 \le \mu_r < 0.022$ $F_p^0 = 1 + 30.55(0.292 - Z_c)^{1.72}$ $0.022 \le \mu_r < 0.075$ $F_p^0 = 1 + 30.55(0.292 - Z_c)^{1.72}[0.96 + 0.1(T_r - 0.7)]$ $0.075 \le \mu_r$ (3.14) F_Q^0 is used only for the quantum gases He, H₂ and D₂ $F_Q^0 = 1.22Q^{0.15} \{1 + 0.00385[(T_r - 12)^2]^{1/M} sign(T_r - 12)\}$ (3.15) Where Q=1.38(He), Q=0.76(H₂), Q=0.52(D₂) Finally, the dense gas viscosity is calculated as: $\eta = \frac{Z_2 F_P F_Q}{s}$ (3.16)

Where
$$\xi = 0.01 \left[\frac{(RT_c)(N_0)^2}{M^3 P_c^4}\right]^{1/6}$$
 (3.17), R=8314.46261815324
J/(kmolK) is universal gas constant N₀=6.02214076x10²⁶
1/(kmol) is Avagadro's constant. Pc is the critical pressure
in kPa, T_c is the critical temperature in degree K, M is

molecular weight in kg/kmol

If data is not available for low pressure thermal conductivity Chung[] equation is used.

Method of Chung et. Al.[19],[20],[5]

$$\frac{k(T)M}{\eta(T)C_{\nu}(T)} = \frac{3.75\psi}{C_{\nu}(T)/R} \quad (3.18)$$

Where

k Thermal conductivity W/(mK)

M molecular weight kg/kmol

 η low pressure gas viscosity Ns/m² Pas

 C_{ν} heat capacity at constant volume kJ/(kmolK)

R universal gas constant 8.3145 kJ/(kmolK)

$$\psi = 1 + \alpha \{ [0.215 + 0.28288\alpha - 1.061\beta + 0.26665Z] / [0.6366 + \beta Z + 1.061\alpha\beta] \} (3.19)$$

$$\alpha = \frac{C_v(T)}{R} - \frac{3}{2} \quad (3.20)$$

$$\beta = 0.7862 - 0.7109\omega + 1.3168\omega^2 \quad (3.21)$$

$$Z = 2.0 + 10.5T_r^2 \quad (3.22)$$

Term β is an emprical correlation and apply only for nonpolar gases. If β value is not available value of 0.758 is assumed.

For High temperature corrections also Chung method is used:

$$k(T,v) = \frac{31.2\eta^0 \psi}{M'} \left[\frac{1}{G_2} + B_6 y + q B_6 y^2 T_r^{1/2} G_2 \right] \quad (3.23)$$

Where η^0 is low pressure viscosity, $M' = Mx10^{-3}$, M is

Class/interface name	Source <u>www.turhancoban.com</u> SCO1.jar					
Interface if_x	Base interface general definition for function f(x)					
Interface if_x	Base interface general definition for function $f0(x0,x1,x2) f1(x0,x1,x2,) \dots$					
Gas_Data	A general class with data of approximately 500 gases. Properties such as critical properties, Pitzer's acentric factor, dipole moment, specific heat at constant pressure, thermal conductivity, viscosity defined.					
Gas_PR1	General EoS definition of gases in Peng-Robinson EOS, utilises Gas_Data class					
Gas_LK	General EoS definition of gases in Lee-Kesler EOS, , utilises Gas_Data class					
Gas_SP	General EoS definition of gases in Schreiber-Pitzer EOS, utilises Gas_Data class					
Gas_PG	General EoS definition of gases in Perfect Gas EOS, utilises Gas_Data class					
Gas	Pure ideal gas EOS including air and other gases					
Plot	2D Plot program					

molecular weight kg/kmol

$$y = \frac{V_c}{6v} (3.24)$$

$$G_1 = \frac{1 - 0.5y}{(1 - y)^3} (3.25)$$

$$G_2 = \frac{(B_1/y)[1 - \exp(B_4y)] + B_2G_1\exp(B_5y) + B_3G_1}{B_1B_4 + B_2 + B_3}$$

The coefficients B_1 to B_7 are functions of the acentric factor ω and dipole moment μ

$$B_i = a_i + a_i \omega + c_i \mu_r^4$$

i	ai	bi	ci
1	2.4166	7.48E-01	-9.19E-01
2	-5.09E-01	-1.5094	-5.00E+01
3	6.6107	5.6207	6.48E+01
4	1.45E+01	-8.9139	-5.6379
5	7.93E-01	8.20E-01	-6.94E-01
6	-5.8634	1.28E+01	9.5893
7	9.11E+01	1.28E+02	-5.42E+01

Other thermodynamic-thermophysical properties calculated by using Schereiber-Pitzer EoS as:

Prandtl number

$$Pr = \frac{C_p \mu}{k}$$

Speed of sound

$$a = \sqrt{-\left(\frac{v^2 C_p}{C_v M}\right) \left(\frac{\partial P}{\partial v}\right)_T}$$

Thermal expansion coefficient

$$\beta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P$$

Isothermal compressibility

$$\beta_T = \sqrt{\frac{\nu}{\left(\frac{\partial P}{\partial \nu}\right)_T}} \quad (3.31)$$

3.0 Computer development and error check

Several programs (classes) in java language to carry out this analysis. The list of program(class) names are given in Table 3.1. The basic properties such as specific heat, thermal conductivities, viscosities of gases defined in class Gas_Data. This class is free of specific equation of state so that it can be used with different EoS such as Lee-Kesler and Perfect Gas. Specific property relations for this developed in **Gas_SP** class. Several other Gas EOS programs are also developed, they will also be listed in the table. All programs are available in <u>www.turhancoban.com</u> internet site for free utilisation by researchers.

Table 4.1 Program lists

A Graphic user interface programs are also given for nonresearchers to utilise these programs. For utilisation of researchers a small sample code is given to show calling of thermodynamic and thermophysical properties for a given state.

You can obtain all properties as an array by using property method. Property method accepts two known thermodynamic property set. Known property sets are as :

Known set	meaning	Known set	meaning		
tp	Temperature	pt	Pressure		
	Pressure		temperature		
vt	Specific volume	tv	Temperature		
	Temperature		Specific volume		
rot	Density	tro	Temperature		
	temperature		density		
pv	Pressure	vp	Specific volume		
	Specific volume		pressure		
pro	Pressure	rop	Density		
	density		pressure		
ph	Pressure	hp	Enthalpy		
	enthalpy		Pressure		
ps	Pressure	sp	Entropy		
-	entropy	_	pressure		
In the following example property pair "tp" is used.					
public static void main(String arg[])					

public static voi { Gas_SP sp=ne	d main(String arg[]) ew Gas_SP("N2");]
sp.mole=false; double T=300; double P=100.0	//Degree K			
sp.print("tp",T,I	P);}			
Properties of N2 n	itrogene Schreiber and Pitzer Eos		- 0	\times
array no	property name	property	unit	
0	P, pressure	100.0	kPA	
1	T, temperature	300.0	deg K	_
3	h enthalny	27 963873781544986	KI/kg	
4	u, internal energy	19.93938568155416	KJ/kg	
5	s, entropy	0.1016123679115501	KJ/kgK	
6	x, quality	2.0	kg vap/kg mix	_
2	Cy, specific heat at con	1.0396977956967528	KJ/kgK KJ/kgK	_
9	a isobaric thermal expan	0.0033336324694642054	1/K	
10	κ isothermal compressib	1.0000071023699687E-5	1/Pa	
11	η Dynamic viscosity	1.787600318502586E-5	Pa.s	
12	k Thermal conductivity	0.027666480768509534	W/mK	_
13	o Surface tension	0.0	N/m	_
15	o density	1 1230711436073273	kg/m ³	_
16	speed of sound	353.0091651518848	m/s	
<pre>double T=300.0 double P=100.0 double a[]=lk.pr for(double x :a) }</pre>	; //degree K ; //kPA operty("tp",T,P); System.out.println(x);		
> "E:\co\java\bin' 100.0 300.0 0.8904155410020 27.963873781544 19.939385681554 0.1016123679115 2.0 1.0396977956967 0.7428905055759 0.003336324694 1.0000071023699	3988 4986 416 5501 7528 9789 4642054 9687E-5			
1.787600318502; 0.027666480768; 0.0 0.6717746743016 1.123071143697; 353.00916515188	586E-5 509534 592 3273 348			

In Table 4.2 different EOS results compared for several thermodynamic states. A Graphic user interface programs are also given for non-researchers to utilise these programs. For utilisation of researchers a small sample code is given to show calling of thermodynamic and thermophysical properties for a given state.

Table 4.2 Comparisons of 4 different EOS for dry Nitrogen

Class	Р	Т	v	h	u	S
Schreiber-	100	300	0.89	27.9	19.9	0.10
Peng-	100	300	0.89	27.9	19.9	0.10
Lee-	100	300	0.89	27.9	19.9	0.10
Perfect_Gas_E	100	300	0.89	27.9	19.9	0.10
Schreiber-	500	300	0.17	27.0	19.9	-
Peng-	500	300	0.17	26.8	19.0	-
Lee-	500	300	0.17	27.1	19.1	-

Perfect_Gas_E	500	300	0.17	27.9	19.9	-
Schreiber-	1000	300	0.08	26.0	19.9	-
Peng-	1000	300	0.08	25.5	17.8	-
Lee-	1000	300	0.08	26.0	18.2	-
Perfect_Gas_E	1000	300	0.08	27.9	19.9	-
Schreiber-	3000	300	0.02	22.1	19.9	-
Peng-	3000	300	0.02	20.5	13.3	-
Lee-	3000	300	0.02	21.9	14.3	-
Perfect_Gas_E	3000	300	0.02	27.9	19.9	-
Schreiber-	5000	300	0.01	18.8	19.9	-
Peng-	5000	300	0.01	15.7	8.93	-
Lee-	5000	300	0.01	18.0	10.4	-
Perfect_Gas_E	5000	300	0.01	27.9	19.9	-

By using equations given above a class called Gas_SP is developed. The result of this class is compared with Lee-KeslerEoS and Perfect results as a mixing of the gases inside air and as a single gas with pseudocritical properties plus ideal gas equation of state. Results are given in table 4.2. It should be note that enthalpies of the perfect gas case (air_PG and Gas) is the same regardless of pressure. In the following figures Peng-Robinson Equation of states is compared with perfect gas equation of state and IAPWS for dry air EOS. IAPWS equation based on the experimental data therefore it can be assumed given carrect values for the range of experimentation. Peng-Robinson equation results are falling between Perfect gas and IAPWS results. This is the expected kind of behevior for such a general EOS based on **accentric factor**.



Figure 4.1 Enthalpy difference of Schereiber-PitzerEoS and Perfect Gas EoS 1000-5000 kPa



Figure 4.2 Enthalpy difference of Schereiber-PitzerEoS and Perfect Gas EoS 100-1000 kPa



Figure 4.3 Entropy difference of Schereiber-PitzerEoS and perfect gas EOS



Figure 4.4 Speed of sound difference of Schereiber-PitzerEoSand perfect gas EOS



Figure 4.5 Enthalpy difference of Schereiber-PitzerEoS and Lee-Kesler EOS



Figure 4.6 Entropy difference of Schereiber-PitzerEoS and Lee-Kesler EOS

4. Conclusions

Thermophysical properties of Pure gases are programmed by using Schereiber-PitzerEoS. This general equation of states are not known much as Lee-KeslerEoS. Lee Kesler.EoSwas a lineer interpolation for two given reference fluids by using Pitzer's Acentric function. As a comparison Schereiber-PitzerEoS is a quadratic least square curve fitting utilising a rich list of gases.

This tool is an important thermodynamic analysis tool for high pressure such as high pressure combustion and other thermodynamic applications. It is also an important tool for heat transfer processes of gases. Since thermophysical properties such as thermal conductivity and viscosity is also calculated both for low and high pressures. In parallel to this work computer model by using Lee-Kesler equation of State, Peng-Robinson Equation of State and ideal gas equation of state is developed. Out of these fourSchereiber-Pitzerequation of state should be the most accurate. It still should be noted that all these equations are general models for better accuracy an actual lab measurement of properties and equation of state developed out of these measurements will be needed, yet as a general form of equations author belives that it will be a valuable tool. It is also possible to use Schereiber-PitzerEoS of pure gases to create real gas mixture models. It will also be used as a base model for combustion process modelling, Gibbs free energy minimisation etc.

All computer codes developed in java programming language and program codes are given as free acess to researchers at internet adress<u>www.turhancoban.com</u>. All equations is given with details and coefficients for researchers wish to develop their own version of computer codes in their desired programming language.

5.	Nomenclatute
Ζ	Compressibility factor
Р	Pressure

ρ	density
R	Gas constant
Т	Temperature
B,C,D,E,F,G	Schereiber-Pitzer EoS constants
T _r	Reduced pressure
T _c	Critical temperature
А	Helmholts energy
Н	Enthalpy
S	Entropy
f	Fugacity
V	Specific volume
Cp	Specific heat at constant pressure
η	Viscosity
k	Thermal conductivity
ξ	Part of vistcosity equation
N_0	Avagadro's number
μ	Dipole moment
Pr	Prandtl's number
а	Speed of sound
β	Thermal expnsion coefficent
β _T	Isothermal compressibility
M	Molecular weight

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