

## Efficient High Pressure Mixture State Equations

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*Abstract* - A method is presented for an accurate noniterative, computationally efficient calculation of high pressure fluid mixture equations of state, especially targeted to gas turbines and rocket engines. Pressures above 1 bar and temperatures above 100K are addressed. The method is based on curve fitting an effective reference state relative to departure functions formed using the Peng-Robinson cubic state equation. Fit parameters for  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , propane, n-heptane and methanol are given.

Keywords: Thermodynamics, State equations, Noniterative, Mixtures

introduction

It is desired that realistic and computationally efficient state equations for fuel/oxidant mixtures be available for design studies of the next generation of gas turbines and rocket engines. In such studies, the state equation plays an important basic, if only partial, role in calculations, where it is used a very large number of times. The equation of state not only provides component partial molar volumes and enthalpies for given pressure, temperature and mass fractions, but also information needed for calculating terms in expressions for mole flux and heat flux vectors. The pressures of interest are high ( $p \geq 1$  Mpa or 10 bar, up to 100 Mpa) and temperatures noncryogenic ( $T \geq 100$  K). Since the critical locus is a function of mole fractions, subcritical and supercritical regions may exist simultaneously and must be handled. Accuracy of the mixture Gibbs function must be sufficient to provide adequate higher order thermodynamic properties such as isentropic

compressibility and thermal expansivity, which have an important effect, direct or indirect, on the fluid mechanical aspect of any design study.

Accurate nonpolar pure substance equations of state (EOS) are frequently based on the Benedict-Webb-Rubin (BWR) form or its modification by Lee and Kesler (Reid, et al, 1987) or on the Helmholtz function (McCarty and Arp, 1991; Muller, et al, 1996). Databases from NIST are based mostly on a modified BWR form, with mixtures using an extended corresponding states algorithm (Friend and Huber, 1994). BWR type equations are not computationally efficient since they have relatively complex nonlinear forms, requiring iteration (sometimes extensive) to calculate molar volume values (Reid, et al, 1987). Also, limits may apply; they should not be used outside tested  $p$  or  $T$  ranges (Reid, et al, 1987). For oxygen and hydrogen, such available EOS have maximum temperature limits that are below the temperatures prevailing in engines. On the other hand, the much simpler cubic state equations (Peng-Robinson or Soave-Redlich-Kwong), while qualitatively correct, do not give accurate volume values (Reid, et al, 1987). For hydrocarbon mixtures, a simple and accurate form based on an extension of the Redlich-Kwong EOS is available (Riazi and Mansoori, 1993). However, it is not clear that this form may be used for mixtures with nonhydrocarbons, particularly oxygen and hydrogen.

In this paper, an accurate and relatively simple noniterative method is described using departure functions based on the Peng-Robinson (PR) state equation. It also allows a reasonable extrapolation from imposed limits to the higher temperatures needed for oxygen and hydrogen. Another advantage is the use of the same functional form for all substances with conventional, coherent mixing rules readily applied to any mixture. This

may be done while utilizing the best available form (possibly distinct) for any particular substance to find the parameters the method requires.

#### Procedure

Departure functions are defined as deviations of thermodynamic functions from a reference state of large molar volume,  $v_u$ . For example, for the Helmholtz free energy,

$$F - F^0 = \int_{v_u}^v p(v', T, x_i) dv' = F_{PR} \quad (1)$$

The  $x_i$  are specie mole fractions. The reference state is that of a perfect gas at a relatively low reference pressure  $p^0$ , so that  $v_u = RT/p^0$ . The Gibbs function is obtained by  $G - G^0 = F - F^0 + pv - 1$ . For a cubic equation of state such as Peng-Robinson:

$$p = RT/(v - b_m) - a_m/(V^2 + 2b_m v - b_m^2), \quad (2)$$

an analytic expression for the pressure integral  $F_{PR}(v_{PR}(T, p, x))$  is readily obtained as well as a direct solution for the molar volume function  $v_{PR}(T, p, x_i)$ . Parameters  $a_m$  and  $b_m$  follow the conventional mixing rules (Reid, et al, 1987; Prausnitz, et al, 1986):

$$a_m = \sum x_i x_j a_{ij}(T), \quad (3a)$$

$$b_m = \sum x_i b_i. \quad (3b)$$

The functions  $a_{ij}(T)$  and constants  $b_i$  are discussed in Appendix A. The PR state equation may have a single real volume root or else multiple real roots near saturation curves. For multiple real roots, the largest and smallest positive roots give gas and liquid

volumes, respectively. Although molar volume values thus obtained may not be accurate, the critical pressure and temperature locus of a mixture may be well estimated using determinants of the matrix of second partial derivatives of the Peng-Robinson free energy with respect to mole fractions (Reid, et al, 1987). Thus despite the weakness of the Peng-Robinson equation in producing correct volume values, it appears that it may be used as a basis for accurate state equation calculations if a volume correction can be provided.

The method proposed here is to first use the departure function formalism for the pure substances of a mixture, and then to reuse it for the mixture as a whole. An accurate calculation is made of the pure substance enthalpy and entropy,  $H$  and  $S$  [e.g., by a Lee-Kesler calculation, Amer. Pet. Inst., 1992) in ranges for which correlations are available. In combination with the Peng-Robinson departure functions, effective reference states are calculated as:

$$H^0(p,T) = H(p,T) - H_{PR}(v_{PR},T), \quad (4)$$

$$S^0(p,T) = S(p,T) - S_{PR}(v_{PR},T), \quad (5)$$

where

$$H_{PR} = pv_{PR} - RT - (a_m - T \partial a_m / \partial T) \ln[(v_{PR} + (1 - \sqrt{2})b_m)/(v_{PR} + (1 + \sqrt{2})b_m)] / (2\sqrt{2}b_m) \quad (6)$$

$$S_{PR} = R \ln[(v_{PR} - b_m)p^0/RT] - \partial a_m / \partial T \ln[(v_{PR} + (1 - \sqrt{2})b_m)/(v_{PR} + (1 + \sqrt{2})b_m)] / (2\sqrt{2}b_m) \quad (7)$$

(Where  $a_m$ , and  $b_m$  are pure substance parameters.) With multiple PR roots, the gas volume is selected for pressures below saturation pressure.

Since the PR state equation is qualitatively correct, the reference state  $H^0$  and  $S^0$  functions are expected to behave similarly to those of a perfect gas. For the substances considered

here, this expectation was met. The following form for  $G^0$  is used to produce very good curve fits:

$$G^0(T,p) = RT_C (a + b/(2T_R) + cT_R - cT_R \ln T_R + 2d\sqrt{T_R}) \quad (8)$$

which gives reference enthalpy and entropy

$$H^0 = T \{ T (a + b/T_R + cT_R - d\sqrt{T_R}) \quad (9)$$

$$S^0 = R(b/(2T_R^2) - e - c(1 + \ln T_R) - d/\sqrt{T_R}) \quad (10)$$

where reduced temperature  $T_R \equiv T/T_C$  and  $a, b, c, d, e$  are cubic polynomials in reduced pressure  $p_R \equiv p/p_C$ . The reference pressure is taken  $p^0 = 1$  bar, and the volume correction is  $v^0 = \partial G^0 / \partial p$ .

At a given pressure, a set of  $T$  values in the available range produces a corresponding set of  $H^0$ . A least squares curve fit then gives  $a, b, c$  and  $d$ . Then a set of  $e$  values is found from SO. consistency requires that  $e$  values are independent of ' $T$ '; for the substances considered, this is essentially satisfied and the mean value is used. (Note that the terms from  $b$  and  $d$  should not be large for the premise of the method to hold.) For oxygen and hydrogen, data is only available up to  $T = 400\text{K}$  (McCarty and Arp, 1991); however, for these substances the behavior of the reference enthalpy at larger temperatures is linear, allowing  $d \equiv 0$ . Figure 1 shows the variation for oxygen. This means that the high temperature behavior mimics that of an ideal perfect gas allowing for reasonable extrapolation of  $H^0$  (and  $G^0$ ) to larger temperatures for  $O_2$  or  $H_2$ . Temperature fits over a set of pressure values followed by cubic polynomial fits to  $a, b, c$  complete the determination of  $G^0$  for the pure substance.

The results indicate that the reference state is essentially that of a perfect gas plus a small correction term. Thus it is assumed that simple ideal mixing rules apply to the reference state, giving:

$$G(T, p, x_i) = F_{PR}(v_{PR}, T) + p v_{PR} - RT + \sum x_i (G_i^0 + RT \ln x_i) \quad (11)$$

where

$$F_{PR} = a_m \ln[(v_{PR} + (1 - \sqrt{2})b_m)/(v_{PR} + (1 + \sqrt{2})b_m)] / (2\sqrt{2}b_m) - RT \ln[(v_{PR} - b_m)p^0 / RT] \quad (12)$$

This assumption is consistent with the use of  $F_{PR}$  to obtain the mixture critical locus independent of the reference state. The fugacity coefficients for the mixture are  $\phi_i = \phi_i^0 \times \phi_{PR,i}$  where:

$$\ln \phi_i^0 = [G_i^0(T, p) - G_i^0(T, 0)] / RT \quad (13)$$

and

$$\ln \phi_{PR,i} = (2 \sum x_j a_{ij} - a_m b_i / b_m) \ln[(v_{PR} + (1 - \sqrt{2})b_m)/(v_{PR} + (1 + \sqrt{2})b_m)] / (2\sqrt{2}b_m RT) - \ln[p(v_{PR} - b_m) / RT] + (p v_{PR} / RT - 1) b_i / b_m \quad (14)$$

Analytical expressions for mixture and component molar volumes, and enthalpies, along with mixture heat capacities, compressibility, and expansivity can be found by differentiation of  $G$  or  $\phi_i$ .

## Results

Curve fit parameters for  $H_2$ ,  $O_2$ ,  $N_2$ , propane, n-heptane and methanol are given in Table 1. (The last fuel has a dipole moment; fits were made to test usage with polar substances.) EOS inputs for the first four are from McCarty and Arp, 1991; the last two use the Lee-Kesler form from Amer. Pet. Inst., 1992.. Good fits for enthalpy and entropy for all

substances were obtained. Table 2 gives the RMS errors relative to mean values for the temperature fits for 11 and S, along with the compression factor  $pV/RT$  and  $c$  value errors. Table 3 provides the temperature and pressure ranges used in the reference fits. Typically, 50 temperature values and 20 pressure values were used. Except for methanol, compression factor estimates have an error of approximately 2% or less. Figures 2 and 3 give enthalpy and density input vs. fit comparisons for  $O_2$ ; similarly, n-heptane values are shown in Figures 4 and 5, methanol values in Figures 6 and 7.

Relatively inferior fits to the lower temperature methanol molar volume values were obtained with errors as large as 17% for liquids. (Due to fit inaccuracies, only quadratic polynomials in pressure were used for methanol.) The problem of fit inaccuracy with methanol can be ascribed to the form of its  $11^\circ$  function. It features a slight 'wiggle' in the 200-600 K temperature range, along with definite positive curvature at high temperatures. A good fit would require a more extensive curve fitting procedure than the one used here, with a function more complex than equation 9. The present procedure, however, is valid for supercritical conditions with  $T \geq 500K$ .

### Summary

The procedure proposed here allows for the use of realistic and computationally efficient equation of state calculations for high pressure gas turbine and rocket engines. It also provides for a reasonable extension to high temperatures of data for  $11_2$  and  $O_2$ . Since the same functional form (based on the Peng-Robinson EOS) is used for all substances, conventional mixing rules are readily applied to any set of components.

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Appendix A  
Peng-Robinson state equation parameters

The constants  $b_i = 0.077796 RT_{Ci}/p_{Ci}$  and the diagonal elements of  $a_{ij}$  are given by

$$a_{ii}(T) = 0.457236 (RT_{Ci})^2 [1 + c_i(1 - \sqrt{T_{Ri}})]^2 / p_{Ci}$$

where  $T_{Ri} \equiv T/T_{Ci}$  and  $C_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$

Parameter  $\omega_i$  is the acentric factor for species  $i$ . The off-diagonal elements are frequently calculated by (Reid, et al, 1987; Prausnitz, et al, 1986):

$$a_{ij} = (a_{ii}a_{jj})^{1/2} (1 - k'_{ij})$$

where  $k'_{ij}$  is an empirical binary interaction parameter. The use of the corresponding states principal during calculations of mixture transport properties requires the use of pseudocritical mixture properties. For these, the following is often used (Reid, et al, 1987; Prausnitz, et al, 1986):

$$v_{Cm} = \sum x_i x_j v_{Cij}$$

$$T_{Cm} = \sum x_i x_j T_{Cij} (v_{Cij} / v_{Cm})$$

$$Z_{Cm} = 0.2905 - 0.085 \omega_m, \text{ or } Z_{Cm} = \sum x_i Z_{Ci} \text{ if the } Z_{Ci} \text{ are known,}$$

$$\omega_m = \sum x_i \omega_i$$

$$p_{Cm} = Z_{Cm} (RT_{Cm} / v_{Cm})$$

where  $T_{Cii} \equiv T_{Ci}$ , etc,

$$T_{Cij} = (T_{Ci} T_{Cj})^{1/2} (1 - k_{ij})$$

$$v_{Cij} = [(v_{Ci}^{1/3} + v_{Cj}^{1/3})^3] / 8$$

$$Z_{Cij} = (Z_{Ci} + Z_{Cj}) / 2$$

$$p_{Cij} = Z_{Cij} (RT_{Cij}/v_{Cij}) .$$

interaction parameters  $k'_{ij}$  and  $k_{ij}$  are not independent, but are related by compatibility for the second virial coefficient (Reid, et al, 1987). Moreover, proper values are important to give the correct mixture fugacity values (Prausnitz, et al, 1986), with small changes significantly affecting results. It is convenient to avoid this complication by relying solely on the pseudocritical parameters by calculating off-diagonal  $a_{ij}(T)$  using the same expression as for the diagonals but with  $T_{Cij}$ ,  $p_{Cij}$ , and  $\omega_{ij} = (\omega_i + \omega_j)/2$ , as was done in Prausnitz, et al, 1986, Chapt. 5, for the Redlich-Kwong equation.

Table 1  
Coefficients of Polynomials

Hydrogen

n	a	b	c	d	e
0	-2.2570E+00	9.3200E+00	3.5559E+00	0.0	-4.2756E+00
1	8.9768E-02	-1.8230E-01	-2.0169E-03	0.0	-9.4720E-03
2	-2.0286E-03	4.1623E-03	9.2431E-05	0.0	3.6176E-04
3	1.3241E-05	-2.6840E-05	-6.8674E-07	0.0	-2.6171E-06

Oxygen

m	a	b	c	d	e
00	-2.6627E-03	-2.6855E-02	3.5256E+00	0.0	-1.8844E+01
11	-5.5055E-02	3.8370E-02	2.3725E-02	0.0	4.8007E-02
22	01.0802E-02	-5.8455E-03	-4.0817E-03	0.0	-7.9077E-03
33	-3.3882E-04	11.7140E-04	1.3537E-04	0.0	2.5601E-04

Nitrogen

n	a	b	c	d	e
0	8.5610E+00	-2.8734E+00	5.2085E+00	-7.3677E+00	-8.8553E+00
1	4.7709E-02	-9.3171E-03	4.9733E-03	-2.8200E-02	2.6602E-02
2	-1.3426E-03	4.4869E-04	-1.4035E-04	9.4103E-04	-7.7410E-04
3	3.8037E-05	-2.1032E-05	2.9341E-06	-2.1826E-05	1.6618E-05

Propane

n	a	b	c	d	e
0	2.2709E+01	-1.7434E+00	3.2680E+01	-4.6968E+01	4.4192E+01
1	-2.1505E-01	1.3190E-02	-2.0673E-01	4.1762E-01	-6.2291E-01
2	-1.2160E-02	1.6696E-03	-3.1790E-03	1.3965E-02	-1.6248E-02
3	6.6740E-04	-7.4289E-05	3.5819E-04	-9.6837E-04	1.2999E-03

N-heptane

n	a	b	c	d	e
0	5.8125E+01	-4.3497E+00	9.0457E+01	-1.2505E+02	1.4930E+02
1	-6.0356E-01	9.9940E-02	-2.3445E-01	7.2965E-01	-8.9921E-01
2	3.0029E-01	-4.9190E-02	1.1821E-01	-3.6738E-01	4.5690E-01
3	-2.0144E-02	3.2149E-03	-8.1978E-03	2.5036E-02	-3.1384E-02

Methanol

n	a	b	c	d	e
0	1.5128E+01	-1.7143E+00	2.0654E+01	-2.8922E+01	1.9287E+01
1	-1.9368E-01	4.7942E-02	-3.6714E-02	1.4502E-01	-1.3353E-01
2	6.5346E-02	-1.2544E-02	2.1425E-02	-7.2466E-02	8.6103E-02

Table 2  
 Maximum RMS Relative Errors  
 (Per cent at fixed pressure)

Substance:	H	S	$pv/RT$	e
Hydrogen	0.23	0.15	1.0	0.35
Oxygen	1.1	0.2	1.4	0.2
Nitrogen	0.22	0.22	0.7	0.6
Propane	2.9	0.5	2.0	0.3
N-heptane	0.26	0.16	2.2	0.1
Methanol	1.35	1.1	10	1.2

Table 3  
 Range of Reference Fits

Substance:	T range (K)	p range (Mpa)
Hydrogen	80-400	0.1-100
Oxygen	100-400	0.1-100
Nitrogen	100-2000	0.1-100
Propane	100-600	0.1-100
N-heptane	210-1500	0.1-27
Methanol	210-1500	1-80

## Figure Captions

- 1) Reference enthalpy for oxygen
- 2) Comparison of input data (symbols) and enthalpy fits for oxygen
- 3) Comparison of input data (symbols) and density fits for oxygen
- 4) Comparison of input data (symbols) and enthalpy fits for n-heptane
- 5) Comparison of input data (symbols) and density fits for n-heptane
- 6) Comparison of input data (symbols) and enthalpy fits for methanol
- 7) Comparison of input data (symbols) and density fits for methanol

Reference Enthalpy for O<sub>2</sub>

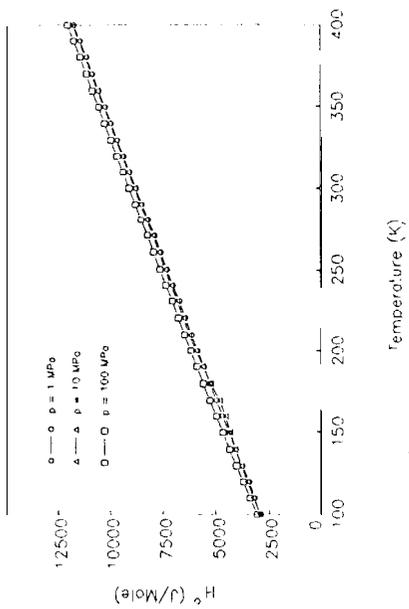


Figure 1

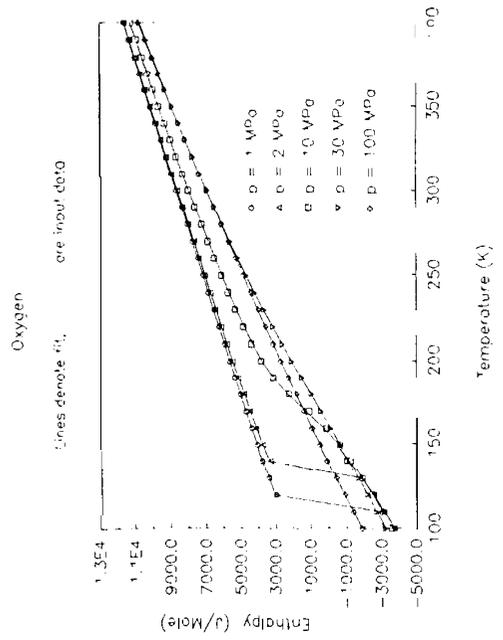


Figure 2

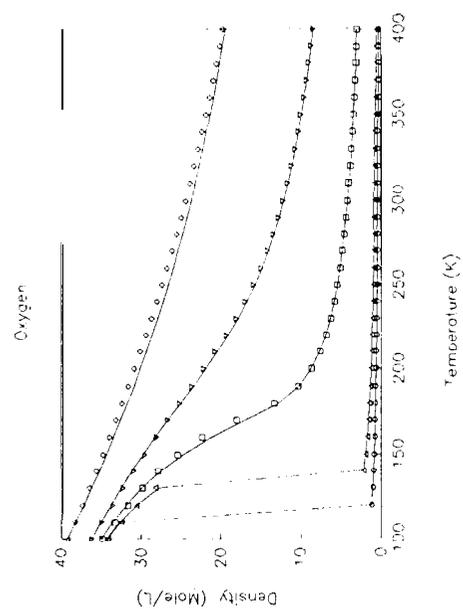


Figure 3

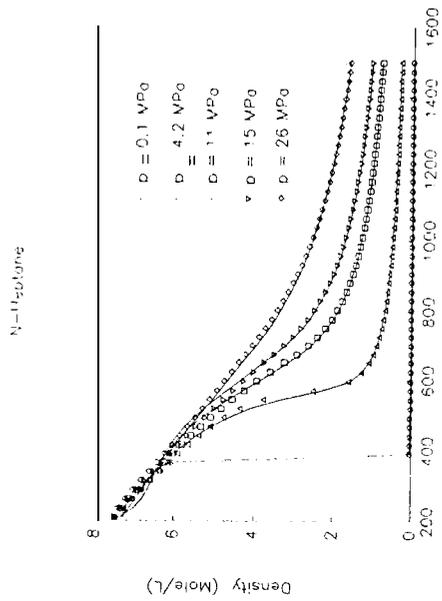


Figure 5

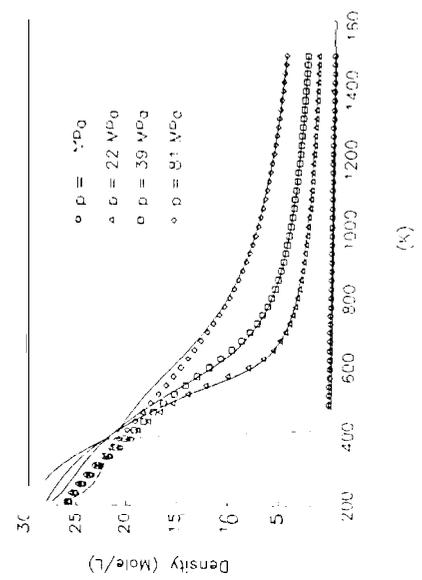


Figure 7

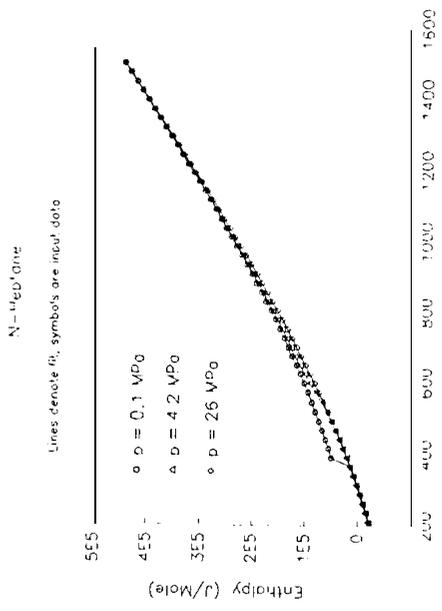


Figure 4

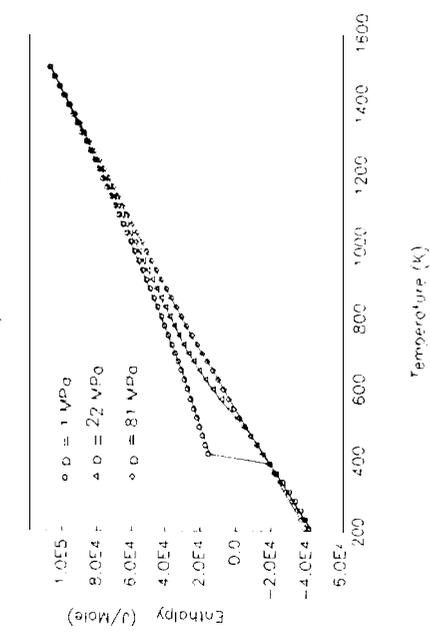


Figure 6