

Modification of the Nonanalytic Equation of State for the Limit of Low Densities*

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As described in previous reports, this equation is constrained to the liquid-vapor coexistence boundary. Integration of the "thermodynamic equation of state" along isotherms involves a term for the compressibility factor of saturated vapor in the limit of low densities, which in previous work was not adequately defined. The present, brief report assumes familiarity with previous work, and presents a solution for the problem, which is to describe saturated-vapor densities in terms of the compressibility factor for saturated vapor, utilizing a given, vapor-pressure equation.

Key words: Equation of state; ethylene; internal energy; saturated vapor densities; thermodynamic properties; vapor pressures.

Symbols and Units

Subscripts *c* and *t* refer to critical and liquid triple points.

Subscript σ refers to liquid-vapor coexistence.

<i>d</i>	density, mol/L
<i>E</i>	the internal energy, J/mol
<i>J</i>	the joule, 1 N·m
<i>L</i>	the liter, 10 ⁻³ m ³
mol	28.054 grams of ethylene (C ¹² scale)
<i>P</i>	pressure in bars, 1 bar \equiv 10 ⁵ N/m ² , (1 atm = 1.01325 bar)
<i>P_σ(T)</i>	vapor pressure, bar
<i>P_σ(ρ)</i>	<i>P_σ[T_σ(ρ)]</i> for equation (1)
<i>R</i>	the gas constant, 8.31434 (J/mol)/K, 0.0831434 (bar·L/mol)/K
<i>R*</i>	(0.0831434)· <i>d_c</i> , bar/K
ρ	<i>d/d_c</i> , reduced density
<i>T</i>	temperature, K
<i>T_σ(ρ)</i>	liquid-vapor coexistence temperature

1. Introduction

Adaptations of this type of equation of state have been described in numerous reports [1–8],¹ which must serve the interested reader as background, to avoid repetition here. The form of this isochoric equation is

$$P - P_{\sigma}(\rho) = \rho R^* \cdot [T - T_{\sigma}(\rho)] + \rho^2 R^* T_c \cdot F(\rho, T), \quad (1)$$

in which, for any given density (isochore), the coexistence

temperature, *T_σ(ρ)*, is obtained by iteration from equations for the orthobaric densities. This is used to obtain the vapor pressure, *P_σ[T_σ(ρ)]*, as a function of density. The function *F(ρ, T)* contains terms roughly analogous to *T* and 1/*T*² of the well-known, Beattie-Bridgeman equation of state, each with a density-dependent coefficient. Symbols and units for this report are given in a list. Fixed-points, used for some examples on ethylene, are given in table 1.

TABLE 1. Fixed-Point Values Used for Ethylene

	Triple Point	Critical Point
Temperature, K	103.97	282.35
Pressure, bar	1.2095·10 ⁻³	50.4234
Density mol/L		
Vapor	1.3994·10 ⁻⁴	7.60
Liquid	23.3590	7.60

2. The Internal Energy

Placing eq (1) in the thermodynamic equation of state yields

$$\Delta E = \int_0^{\rho} [(Z_{\sigma}(\rho) - 1) \cdot RT_{\sigma}(\rho)/\rho + \dots] \cdot d\rho, \quad (2)$$

where *E* is the internal energy.

Our problem is in the definition and value of

$$Z_{\sigma}(\rho) \equiv P_{\sigma}(\rho)/[\rho \cdot R^* \cdot T_{\sigma}(\rho)]$$

in the limit of low densities, because equations for the vapor pressures, *P_σ(T)*, and for the saturated vapor densities, *ρ_σ(T)*, generally are independent. From equations which we

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¹ Figures in brackets refer to literature references at the end of this paper.

used for propane, for example [6], we find that at $\rho = 0$, (hence $T_\rho(\rho) = 0$), the value of $Z_\sigma(\rho)$ may range from 0 to ∞ . Even if $Z_\sigma(\rho) \rightarrow 1$ at low densities, there remains the problem of loss of significant digits in the difference $[Z_\sigma(\rho) - 1]$.

3. Saturated Vapor Densities

A solution for the problem of eq (2) is to describe saturated vapor densities in terms of their compressibility factors (utilizing the vapor-pressure equation) in such a way that the integrand in eq (2) will extrapolate to a reasonable value as $\rho \rightarrow 0$.

The following formulation utilizes temperature, T , as independent variable. If, for a given vapor density, however, the temperature has been found from this formulation by iteration, then $T \rightarrow T_\sigma(\rho)$, and the compressibility factor becomes a function of density, $Z_\sigma(T) \rightarrow Z_\sigma[T_\sigma(\rho)]$, as needed for eq (2), above.

Define the constant $A_0 \equiv (Z_c - 1)$, where $Z_c \equiv P_c/(\rho_c \cdot R^* \cdot T_c)$ is value of the compressibility factor at the critical point, and the reduced variables,

$$\Pi(T) \equiv P_\sigma(T)/P_c, x(T) \equiv T/T_c, u(T) \equiv 1 - x,$$

when the equation for saturated vapor densities,

$$\rho_\sigma(T) \equiv P_\sigma(T)/[Z_\sigma(T) \cdot R^* \cdot T] \quad (3)$$

is given by

$$Z_\sigma(T) = 1 + A_0 \cdot \Pi \cdot x^{-2} \cdot f(x), \quad (4)$$

$$f(x) \equiv 1 + A_1 \cdot u^\epsilon + \sum_{i=2}^5 A_i \cdot u^{i-1}. \quad (5)$$

At $T = 0$, $f(x)$ is finite, and $Z_\sigma(T) = 1$, due to the exponential dependence of the vapor pressure, $P_\sigma(T) \sim \exp(-1/T)$.

To give substance to these analytical results, we present the vapor-pressure equation for ethylene in appendix A, taken from an unpublished report. Figure 1 shows behavior of $f(x)$, eq (5), for which the constants are

$$\epsilon = 0.36 \quad A_3 = 0.6955 \ 385$$

$$A_1 = -0.8648 \ 073 \quad A_4 = -3.0648 \ 51$$

$$A_2 = 0.8931 \ 234 \quad A_5 = 5.8633 \ 40$$

The *rms* relative deviation of the ethylene saturated vapor densities is 0.07 percent for a total of 29 points, including experimental data from 233 through 282 K, and data from 120 through 220 K derived via the vapor-pressure and virial equations [7].

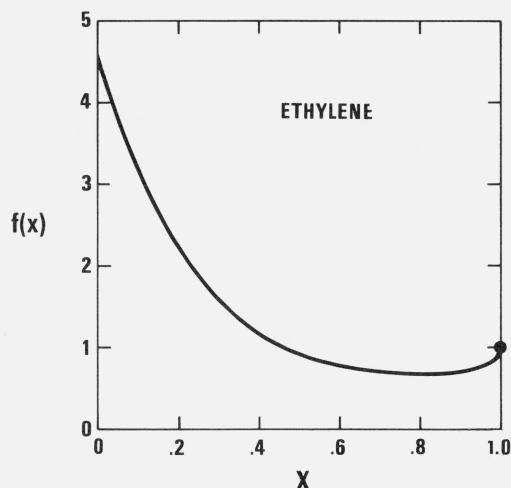


FIGURE 1. Behavior of $f(x)$, eq (5), for ethylene.

4. Conclusions

By use of eqs (3) and (4) for substitutions in eq (2) at densities $\rho \leq \rho_c$, one obtains

$$\Delta E = \int_0^\rho [(Z_c - 1) \cdot (Z_\sigma(\rho)/Z_c) \cdot RT_c \cdot f(x) + \dots] \cdot d\rho, \quad (2a)$$

in which the integrand is finite in the limit $\rho = 0$, ($T_\sigma(\rho) = 0$).

Because the equation of state is nonanalytic, the integrations of eqs (2) or (2a) must be performed numerically. In published works [4,5,6] we have not called upon the equation of state at densities so very low as to encounter the difficulty described and resolved in this report. At very low densities, the saturated vapor temperature diminishes roughly only as the logarithm of density, $1/T \sim \ln(1/\rho)$.

As it is improbable that we ever shall be privileged to compare thermodynamic properties from eq (2) with those from eq (2a), our objective in this report has been to describe the problem, and to give a solution for consideration in all future work.

5. Appendix A. Ethylene Vapor-Pressure Equation

For use in eq (3), above, our unpublished vapor-pressure equation for ethylene, from the triple- to the critical-point, for P in bar, is

$$\ln(P) = a + b \cdot u + c \cdot x + d \cdot x^2 + e \cdot x^3 + f \cdot x \cdot (1 - x)^\epsilon, \quad (1A)$$

with arguments $x \equiv (T - T_t)/(T_c - T_t)$, $u \equiv (1 - T_t/T)/(1 - T_t/T_c)$, where $\epsilon = 1.30$, and

$$\begin{aligned} a &= -6.717\,5716 & d &= 4.553\,6920 \\ b &= 13.897\,6040 & e &= -1.132\,0564 \\ c &= -6.681\,2125 & f &= 0.623\,6504 \end{aligned}$$

For 38 data points from 104.9 through 282.3 K, the *rms* of relative pressure deviations is 0.04 percent [7].

6. References

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