A Vapor Pressure Equation from Extended Asymptotic Behavior

The vapor pressure equation proposed here possesses several interesting features and does an excellent job representing data. The currently accepted theoretical behavior in the regions of the triple point and the critical point are intrinsic features of the expression. The equation is valid over the entire range from the triple point to the critical point and yet possesses only three adjustable constants. Results are presented for a small but chemically diverse set of compounds. This work represents an extension of the Churchill-Usagi correlation technique from heat transfer and fluid mechanics to thermodynamics.

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Introduction

Vapor pressure equations represent the pressure-temperature behavior of pure substances along their vapor-liquid saturation boundary. Accurate vapor pressures are important in the design of chemical processes, in the development of isochoric equations of state, and in obtaining thermodynamic properties tables for pure substances.

Many vapor pressure equations have appeared in the literature. Unfortunately, equations that are accurate often do not describe the entire vapor pressure curve, but do contain several adjustable constants (up to seven, Ambrose et al., 1970). A mathematical expression that describes the vapor pressure as a function of temperature along the entire vapor-liquid curve has been the objective of extensive studies using both theoretical and empirical approaches.

Goodwin (1969) included nonanalytic behavior at the critical point and presented vapor pressure equations for oxygen and nitrogen. Ambrose et al. (1970) developed a vapor pressure expression using Chebyshev polynomials; their expression required up to seven constants to obtain good agreement with experimental data. Wagner (1973) proposed a stepwise procedure that optimizes selection of a functional form of an equation for each substance. His expression included nonanalytic behavior in the critical region along with several background terms.

Another group of equations encompasses generalized vapor pressure expressions. These equations require knowledge of the critical and boiling point temperatures and one or more physical properties to determine the constants. The main disadvantage of these equations is that they generally fail to describe the critical region adequately. Examples of such equations include those of Miller (1965), Frost and Kalkwarf (1953), and Gomez-Nieto and Thodos (1977, 1978). Reid et al. (1977) summarize other vapor pressure equations.

This paper presents a vapor pressure equation that has a minimal number of parameters, adequately represents the behavior of many diverse substances with a single form, has identifiable theoretical bases, and introduces the Churchill and Usagi (1972) technique for thermodynamic correlations. The new equation provides vapor pressures accurate to 0.1% with only one empirical term.

Selection of Variables

The selection of independent and dependent variables plays an important role in the development of a vapor pressure equation. For example, when the logarithm of pressure is plotted against inverse absolute temperature, the curves for various fluids intersect, Figure 1. This is an indication that the curve is not a general function even though it is almost linear. Equations using these variables are accurate only over certain regions of the vapor pressure curve. The equation proposed here uses dimensionless pressure and temperature variables of the form:

$$t = \frac{T - T_t}{T_c - T_t} \tag{1}$$

$$p = \frac{P - P_t}{P_c - P_t} \tag{2}$$

Plots of p as a function of t for various substances appear in Figure 2. The curves do not intersect, they have the same general

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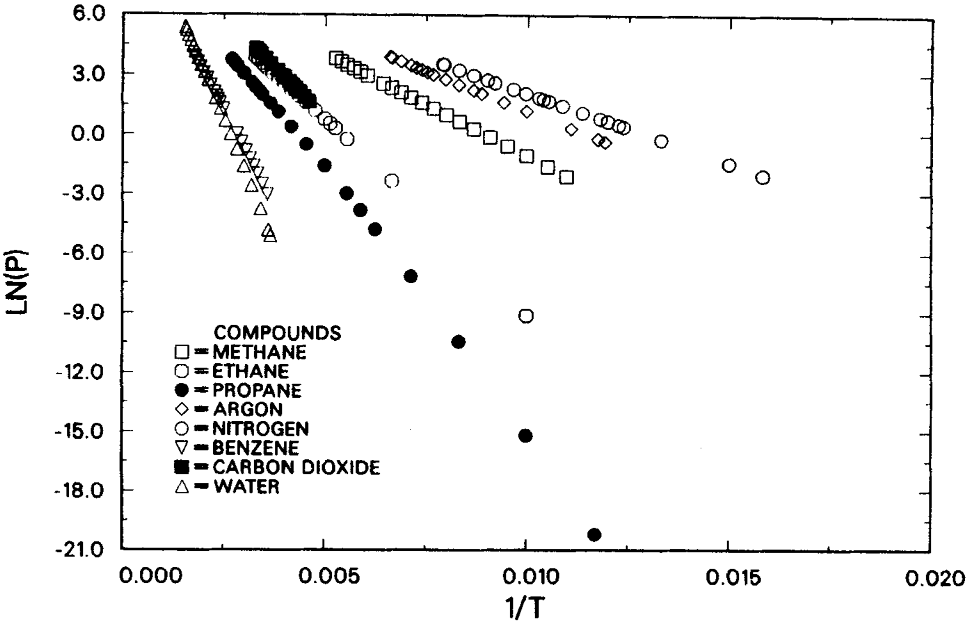

Figure 1. Inverse temperature dependence of log vapor pressure of several liquids.

shape, and their location varies monotonically with the length of the vapor pressure curve. Thus, a general function relating p and t should exist.

Theoretical Development

The Clapeyron equation relates the slope of the vapor pressure curve to changes in enthalpy and volume upon vaporization

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \tag{3}$$

where ΔH is the enthalpy of vaporization and ΔV is the difference between the vapor and liquid molar volumes at saturation. Assuming the vapor volume to be that of an ideal gas and much larger than the liquid volume produces the Clausius-Clapeyron equation:

$$\frac{d\ln P}{dT} = \frac{\Delta H}{RT^2} \tag{4}$$

Finally, assuming a weak temperature dependence for the enthalpy of vaporization near the triple point produces

$$\frac{d\ln P}{dT} = \frac{b_1 + b_0(T - T_t)}{RT^2} \tag{5}$$

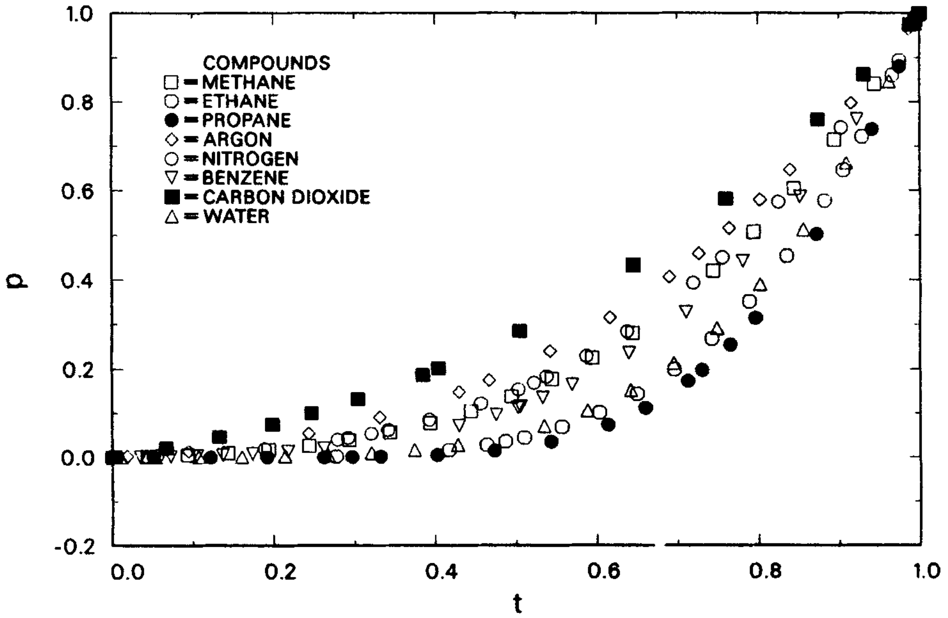

Figure 2. Temperature dependence of vapor pressures of several liquids when expressed as dimensionless variables.
Variables p and t defined in text

The assumptions leading to Eq. 5 all are adequate in the vicinity of the triple point. Transformation to the variables p and t and integration produces:

$$p = p_0 = a_0 + a_1(a_3 t + 1)^{b_0/R} \exp\left(\frac{-a_2 + b_0/R}{a_3 t + 1}\right) \quad (6)$$

where

$$a_0 = \frac{-P_t}{P_c - P_t} \quad (7)$$

$$a_1 = -a_0 \exp(a_2 - b_0/R) \quad (8)$$

$$a_2 = \frac{b_1}{RT_t} \quad (9)$$

$$a_3 = \frac{T_c - T_t}{T_t} \quad (10)$$

and p_0 denotes the dimensionless vapor pressure as the temperature approaches triple point value. In effect, p_0 establishes the asymptotic behavior at the triple point.

Scaling theory (Levelt-Sengers et al., 1969, 1977; Griffiths, 1965) provides an economical representation of the critical region behavior. Vapor pressure equations based upon scaling laws must satisfy

$$\frac{d^2P}{dT^2} \sim (T - T_c)^{-\Theta} \quad (11)$$

which implies divergence as T approaches T_c. Scaling theory postulates that the value for the exponent Θ should be about 0.1. In this work we assume that the second derivative of the vapor pressure with respect to the temperature behaves in the critical region as

$$\frac{d^2P}{dT^2} = K_1(T_c - T)^{-\Theta} + K_2(T_c - T) + K_3(T_c - T)^2 \quad (12)$$

Upon conversion to p and t, Eq. 12 becomes

$$\frac{d^2p}{dt^2} = k_1(1 - t)^{-\Theta} + k_2(1 - t) + k_3(1 - t)^2 \quad (13)$$

Double integration of Eq. 13 provides

$$p = \frac{k_1}{2 - \Theta}(1 - t)^{2-\Theta} + (k_2/6)(1 - t)^3 + (k_3/12)(1 - t)^4 + a_4 t + C \quad (14)$$

To evaluate the integration constant c requires the condition of the critical point, $p = 1$ at $t = 1$, and Eq. 14 becomes

$$p = p_\infty = 1 - a_4(1 - t) + a_5(1 - t)^{2-\Theta} + a_6(1 - t)^3 + a_7(1 - t)^4 \quad (15)$$

where p_∞ denotes the dimensionless vapor pressure as the temperature approaches the critical point value. In effect, p_∞ establishes the asymptotic behavior at the critical point. Churchill and Usagi (1972, 1974) proposed the generalized use of Fermat's Last Theorem (Ribenbaum, 1979) to correlate data:

$$y^N(x) = y_0^N(x) + y_\infty^N(x) \quad (16)$$

where

$y_0(x)$ = asymptote as x approaches 0
$y_\infty(x)$ = asymptote as x approaches ∞
N = arbitrary exponent

This expression introduces only one arbitrary parameter and, according to Churchill (1983), measures the deviation of the data from that of the theoretical asymptotes.

Obviously, we can use Eq. 16 in conjunction with Eqs. 6 and 15 to develop a vapor pressure equation. However, we must adjust the constants slightly to accommodate the Churchill-Usagi technique, and thus the asymptotes become:

$$p_0(t) = a_0 + a_1(a_3 t + 1)^{b_0/R} \exp\left(\frac{-a_2 + b_0/R}{a_3 t + 1}\right) \quad (16)$$

Table 1. Sources of Vapor Pressure Data

Compound	No. of Points	Source
Methane	112	Prydz & Goodwin (1972) Jansoone et al. (1970)
Ethane	130	Douslin & Harrison (1973) Pope (1971) Straty (1976b) Ziegler et al. (1964)
Propane	89	Beattie et al. (1937) Douslin & Harrison (1976) Kratzke (1980) Kemp & Egan (1938) Goodwin (1972)
Argon	57	Wagner (1973)
Nitrogen	67	Wagner (1973)
Benzene	42	Ambrose (1981) Ambrose et al. (1969) Wilhoit & Zwolinski (1971)
Carbon dioxide	130	Levelt-Sengers & Chen (1972) Meyers & Van Dusen (1933) Michels et al. (1950)
Water	—	Haar et al. (1984)
Fluorine	120	Prydz & Straty (1973)
n-Butane	80	Haynes & Goodwin (1982)
Hydrogen sulfide	72	Goodwin (1983)
Total points	987	

Table 2. Critical and Triple Point Values for Substances

Compound	$\frac{T_c}{K}$	$\frac{T_t}{K}$	$\frac{P_c}{MPa}$	$\frac{P_t}{kPa}$	Sources
Methane	190.53	90.66	4.5955	117.030	Prydz & Goodwin (1972) Armstrong et al. (1955)
Ethane	305.33	90.348	4.87140	1.1308×10^{-3}	Douslin & Harrison (1973) Goodwin (1976)
Propane	369.85	85.470	4.24709	1.6808×10^{-7}	Das & Eubank (1973) Goodwin (1982) Thomas & Harrison (1982)
Argon	150.86	83.78	4.89790	68.7	Angus & Armstrong (1972)
Nitrogen	126.2	63.148	3.4002	12.52	Wagner (1973)
Benzene	562.161	278.678	4.8982	4.782	Ambrose (1981) Ambrose et al. (1967) Wilhoit & Zwolinkski (1971)
Carbon dioxide	304.21	216.58	7.3825	518.5	Ely (1985)
Water	647.126	273.16	2.2055	0.61173	Haar et al. (1984)
Fluorine	144.51	53.4811	5.215	0.252	Prydz & Straty (1973)
n-Butane	425.16	134.86	3.796	6.7358×10^{-4}	Haynes & Goodwin (1982)
Hydrogen sulfide	373.4	187.66	9.008	23.20	Goodwin (1983)

where

$$a_0 = 1 - \frac{P_t}{P_c - P_t}$$

$$a_1 = -(a_0 - 1)\exp(a_2 - b_0/R)$$

$$a_2 = b_1/RT_t$$

$$a_3 = \frac{T_c - T_t}{T_t}$$

and

$$p_\infty(t) = 2 - a_4(1 - t) + a_5(1 - t)^{2-\Theta} + a_6(1 - t)^3 + a_7(1 - t)^4 \quad (17)$$

The new vapor pressure equation becomes:

$$p(t) = [p_0(t)^N + p_\infty(t)^N]^{1/N} \quad (18)$$

where

$$p(t) = 1 + \frac{P - P_t}{P_c - P_t}$$

$p_0(t)$ = asymptotic behavior of the vapor pressure curve near the triple point, Eq. 6

$p_\infty(t)$ = asymptotic behavior of the vapor pressure in the critical region, Eq. 17

N = empirical constant

Equation 18, which describes the entire vapor pressure curve within experimental accuracy, contains eight parameters (Θ, N, b_0, b_1, a_4, a_5, a_6, and a_7) that must be determined from experimental data.

Experimental and smoothed data for eight substances (CO_2, Ar, CH_4, C_2H_6, C_3H_8, N_2, C_6H_6, and H_2O) have been used to establish the new equation. Carbon dioxide and propane represent the limits of short and long vapor pressure curves, respectively. The other substances represent simple molecules (Ar, CH_4), quadrupolar molecules (C_2H_6, N_2), polar molecules (H_2O), and complex molecules (C_6H_6).

Determination of Constants

The experimental and smoothed data used to test the new equation come from the sources listed in Table 1. The values used for triple point and critical point properties appear in Table 2, along with the sources.

The high degree of correlation between some of the parameters in Eq. 18 precludes simultaneous determination of all parameters by nonlinear, weighted least-squares parameter estimation methods. Walton et al. (1978) suggest that $\Theta = 0.199$ provides the optimal representation of experimental vapor pressure data for CO_2, C_2H_6, C_2H_4, He_4, CH_4, O_2, and H_2O in the critical region. We therefore have chosen a fixed value of $\Theta = 0.2$ for this work. The empirical parameter N results from a parametric fit.

The remaining parameters were determined using the multivariate secant method (Ralston and Jennrich, 1979), a variation of the Gauss-Newton method (Hartley, 1961), together with a Levenberg-Marquardt method (Levenberg, 1944; Marquardt, 1963). The experimental points received weights proportional to p^{-2} to reflect the observations of Levelt-Sengers (1970). The

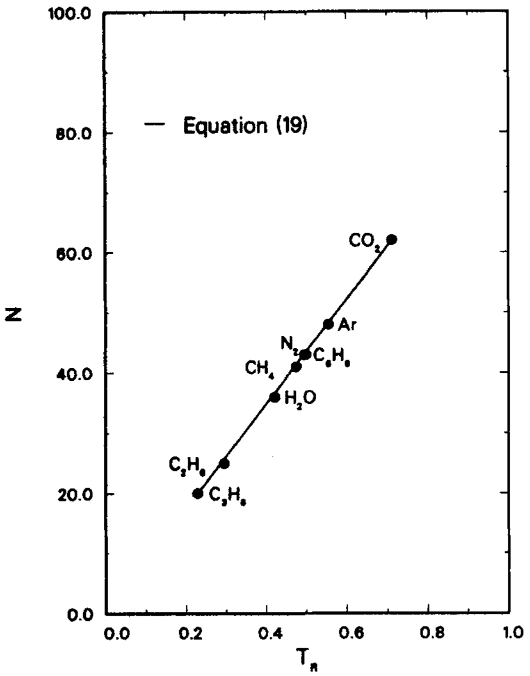

Figure 3. Relation between empirical exponent *N*, Eq. 18, and reduced triple point temperature for several substances.

parametric determination of N consisted of repeating the nonlinear fit procedure for various fixed values of N to achieve a minimum sum of weighted squares.

Figure 3 contains the values of N determined for each substance. The values of N vary linearly with reduced triple point temperature and may be represented well by

$$N = 87\ T_{tr} \tag{19}$$

Simple relations also exist among the a_i:

$$a_5 = -0.11599104 + 0.29506258\ a_4^2 - 0.00021222\ a_4^5 \tag{20}$$

$$a_6 = -0.01546028 + 0.08978160\ a_4^2 - 0.05322199\ a_4^3 \tag{21}$$

$$a_7 = 0.05725757 - 0.06817687\ a_4 + 0.00047188\ a_4^5 \tag{22}$$

Table 3. Parameters for New Vapor Pressure Equation

Compound	a_4	b_0	b_1
Methane	3.15902305	−19.36816406	8799.13964844
Ethane	4.58003599	−36.78014671	17889.46289040
Propane	5.20400360	−43.62539091	24765.10829288
Argon	2.66553020	−15.72202396	6742.03613280
Nitrogen	3.06597185	−23.52451515	6103.60400391
Benzene	3.50497763	−47.00322562	35012.52391391
Carbon dioxide	2.17343688	−25.84003488	16917.72460938
Water	4.51695585	−38.34726715	45025.30078125
Fluorine	3.93097138	−30.43794551	7503.608737
n-Butane	4.77783243	−46.12413389	28712.930787
Hydrogen sulfite	3.20451811	−29.00972909	19735.314538

After imposing Eqs. 19–22 and setting $\Theta = 0.2$, only three adjustable parameters, a_4, b_0, and b_1, remain in the vapor pressure equation. Table 3 contains the values of these parameters determined from the experimental data and Eqs. 18–22.

Results

Table 4 presents the absolute and relative deviations obtained by fitting various other models to the eight-substance data base used to develop the current equation. In general, the results tend to favor the current equation and those of Goodwin and Wagner. The advantage of the current equation is that it contains fewer adjustable parameters.

The new equation has an average overall relative error of 0.05%, ranging from 0.02% for CO_2 to 0.14% for propane. However, the major contributions to the propane average come from the very low pressures, which are not measured but rather calculated values (Goodwin, 1980). When considering only experimental data for propane, the average relative deviation falls to 0.05%. The data of Goodwin (1980) emphasize the utility of the new equation for vapor pressures as low as 1 μPa. The average percentage error for water is calculated from the smoothed data given by Haar et al. (1984). This source differs by less than 12 parts in 100,000 from the experimental data of Guildner et al. (1976), Stimson (1969), and Osborne et al. (1933).

Table 5 presents comparisons of the absolute and relative deviations for H_2S, *n*-butane, and F_2. The fit of Eq. 18 utilizes only three parameters for this test, while the other models are

Table 4. Average Deviations between Experimental Values and Fits of Various Models to Data Base

	Equation and Deviations											
	Gomez-Nieto Thodos		Riedel et al.		Frost & Kaulkwarf		Goodwin		Wagner		Eq. 18	
Substance	Abs	Rel	Abs	Rel	Abs	Rel	Abs	Rel	Abs	Rel	Abs	Rel
Methane	0.0110	0.0992	0.0553	0.4217	0.0127	0.0952	0.0029	0.0172	0.0033	0.0171	0.0053	0.0448
Ethane	0.0214	0.1456	0.0599	0.4202	0.0182	0.1161	0.0098	0.0431	0.0104	0.0504	0.0111	0.0595
Propane	0.0508	0.8837	0.0258	1.5935	0.0672	0.7165	0.0046	0.0510	0.0056	0.0832	0.0038	0.1423
Argon	0.0063	0.0465	0.0422	0.3041	0.0117	0.0463	0.0021	0.0250	0.0017	0.0157	0.0034	0.0266
Nitrogen	0.0068	0.0811	0.0356	0.3681	0.0060	0.0343	0.0011	0.0154	0.0014	0.0170	0.0018	0.0308
Carbon dioxide	0.0196	0.0367	0.0512	0.1474	0.0235	0.0464	0.0050	0.0176	0.0183	0.0326	0.0071	0.0238
Benzene	0.0089	0.1164	0.0164	0.1781	0.0183	0.1936	0.0015	0.0190	0.0017	0.0182	0.0059	0.0645
Water	0.0387	0.0540	0.2504	0.5458	0.6485	0.7527	0.0043	0.0059	0.0152	0.0229	0.0210	0.0512
Total avg.	0.0204	0.1829	0.0671	0.4974	0.1008	0.2501	0.0039	0.0243	0.0072	0.0321	0.0074	0.0554

Abs, average absolute deviation; Rel, average relative deviation.

Table 5. Average Deviation between Experimental Values and Models when Duty-Fitting Characteristic Constants

	Equation and Deviations											
	Gomez-Nieto Thodos (a)		Riedel et al. (b)		Frost & Kaulkwarf (c)		Goodwin (d)		Wagner (e)		Eq. 18 (f)	
Substance	Abs	Rel	Abs	Rel	Abs	Rel	Abs	Rel	Abs	Rel	Abs	Rel
Hydrogen sulfide	0.0471	0.1323	0.0897	0.3622	0.0405	0.1213	0.0365	0.1048	0.0425	0.1178	0.0447	0.1185
n-Butane	0.0146	0.2298	0.0172	0.6608	0.0139	0.3535	0.0133	0.1311	0.0129	0.1364	0.0164	0.1807
Fluorine	0.0186	0.2349	0.0554	0.4312	0.0211	0.1695	0.0072	0.0754	0.0053	0.1181	0.0063	0.1221
Total avg.	0.0268	0.1990	0.0541	0.4847	0.0252	0.2148	0.0192	0.1038	0.0202	0.1241	0.0225	0.1404

Abs, average absolute deviation; Rel, average relative deviation
No. of characteristic constants: (a) 3, (c) 5, (d) 5, (e) 4, (f) 3; (b) predictive

fitted to the various data sets. Once again, the new equation compares favorably with the other models.

Finally, Figure 4 presents a typical deviation plot comparing experimental data with Eq. 18. In this case the data are those of ethane.

Discussion

The new vapor pressure equation presented here provides accuracy comparable with that of the models of Gomez-Nieto and Thodos; Riedel et al.; Frost and Kalkwarf; Goodwin; and Wagner. The advantages of the new equation are a single generalized form for all substances that satisfies existing theories in both limits, and only three adjustable parameters.

Because the formulation is based upon known physical behavior, the adjustable parameters reflect physical properties of the substance. The parameter a_4 is proportional to the Riedel constant, while b_1 is proportional to the enthalpy of vaporization at the triple point. These physical associations imply that the new equation may provide predictive as well as correlative capabilities. This report demonstrates the correlative capability; the predictive generalization is the subject of a continuing investigation.

This work shows that our new vapor pressure equation can correlate accurately the behavior of the homologous alkane series, polar and nonpolar compounds. It also demonstrates that Fermat's Last Theorem provides a powerful tool for the development of theoretically based correlations not only in heat transfer and fluid mechanics, but also in thermodynamics.

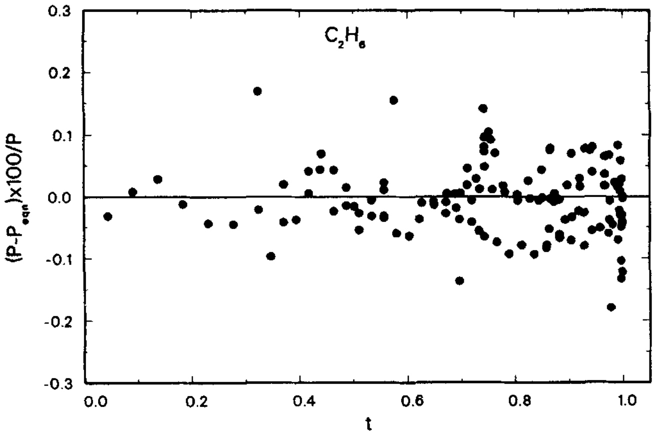

Figure 4. Deviations of experimental observations of vapor pressures for pure ethane from the best fit using Eq. 18.

Experimental data are summarized by Goodwin, et al. (1976).

Acknowledgment

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Notation

a_j = constants for new vapor pressure equation, Eqs. 6, 17, 18, $j = 0, 7$
b_j = characteristic constants for new vapor pressure equation, Eqs. 6, 17, 18, $j = 0, 1$
c = integration constant
H = enthalpy
K_j = constants, Eq. 12
k_j = constants, Eq. 13
N = empirical constant of new vapor pressure equation
p = reduced vapor pressure variable
p_0 = asymptotic vapor pressure behavior in triple point region, Eq. 6
p_∞ = asymptotic vapor pressure behavior in critical point region, Eq. 15
P = vapor pressure
P_c = critical pressure
P_t = triple point pressure
R = universal gas constant
t = reduced temperature variable
T = temperature
T_c = critical temperature
T_r = reduced temperature, T/Tc
T_t = triple point temperature
V = molar volume
y_0 = asymptote for small values
y_∞ = asymptote for large values
Δ = change between vapor and liquid phases
Θ = exponent for vapor pressure divergence

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