A NEW SCALED-VARIABLE-REDUCED-COORDINATE FRAMEWORK FOR CORRELATION OF PURE FLUID SATURATION PROPERTIES

By

RONALD DAVID SHAVER

Bachelor of Science

Oklahoma State University

Stillwater, Oklahoma

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Thesis Approved:

K.A.M.Gasem
Thesis Adviser

Jan Wagner

Robert Robinson Jr

Norman N. Durham
Dean of the Graduate College

PREFACE

A new scaled-variable-reduced-coordinate framework for the correlation of pure fluid saturation properties was developed. Correlations valid over the entire saturation range from the triple point to the critical point were developed for correlation of vapor pressures, liquid densities and vapor densities of widely varying compounds. The correlations are consistent with scaling theories in the near-critical region, and compare favorably with the existing literature models. The three correlations were extended to generalized models to provide predictive capability with average absolute deviations within 1.5%.

I wish to express my sincere appreciation to my adviser, Dr. K. A. M. Gasem, for his assistance and support during the course of this study. If it were not for his continued enthusiasm in his work and his ongoing interest in his students, much of this work would not have been completed.

I would like to thank the members of my graduate committee, Dr. R. L. Robinson, Jr. and Dr. J. Wagner, for their time and their suggestions about this work.

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NOMENCLATURE

Symbols

A,B,C	correlation constants
B	critical point scaling exponent
a,b	parameters in Equations 11-13
f	functions used in vapor pressure generalization
H	enthalpy
p	vapor pressure
T	temperature
v	volume
X	correlating variable
Y	saturation property
Z	compressibility factor
RMSE	root mean square error
%AAD	average absolute percent deviation
SS	objective function defined by Equation (27)

Greek Symbols

α	correlation scaling exponent and exponent of Equations 12-13
β	scaling law exponent (Equations 11-13)
Δ	change in property
$\Delta\alpha$	α_c-α_t
ϵ	reduced variable for property X
ρ	density
ϕ	order parameter
Θ	correlating function
τ	reduced temperature defined as $(T_c-T)/T_c$
Ψ	correction terms in vapor pressure generalization
ω	acentric factor

Subscripts

b	normal boiling point state
c	critical point state
i	initial point
r	reduced property
s	simple fluid
t	triple point state
σ	state of saturation
calc	calculated
exp	experimental

CHAPTER I

INTRODUCTION

The saturation properties of pure fluids play a major role in both the theoretical understanding of fluid phase behavior and in the design and operation of a multitude of industrial processes. Such properties are essential both when used directly in calculations, or when used as input to a variety of models and applications.

Because pure fluids represent the limiting conditions of mixtures, such properties are essential to vapor-liquid equilibrium calculations of multi-component systems. The importance of adequate property correlations is evident when a derived quantity such as dp/dT is needed, or when equation of state parameters are required. For example, accurate pure-fluid saturation properties are needed to estimate input variables (e.g., T_c, p_c, ω) for a number of generalized-parameter equations of state that have been developed to facilitate generalized predictions of mixture properties (1,2,3).

Although the literature contains many correlations (4-8) for predicting saturation properties, many of these correlations suffer from a limited range of applicability and poor suitability for generalization. Furthermore, the need for specialized correlations for each saturation property amplifies the usefulness of an efficient and reliable unified framework for the prediction of saturation properties.

The majority of the existing correlations are based on one of two approaches: equations of state (4,5,9) which attempt to relate the p,v,T behavior over the entire fluid region, or corresponding states theory (CST) (10-14) which relates two specific thermodynamic variables in the saturated region. In general, while equations of state are more efficient in correlating thermodynamic properties, they are incapable of accurately predicting a number of saturation properties of vapor and liquid phases simultaneously. Because of this inadequacy, the CST method has been more successful. The present work utilizes the CST concepts to develop a unified framework for the correlation of saturation properties.

The goal of this work was to develop a framework for the proper reduction and correlation of saturated properties over the entire bounded saturation region. More specifically, work was directed at correlation of properties of saturated pure fluids over a temperature range extending from the triple point to the critical point. The characteristics of the desired framework are:

(1) ability to correlate a number of saturation properties (at the desired precision) over the full saturation range from the triple point to the critical point,

(2) ability to satisfy established theoretical limiting behavior for the properties considered,

(3) ability to predict the behavior of fluids of widely varying chemical nature,

(4) suitability for generalization to provide predictive capability, and

(5) simplicity.

This study involves the development of the general framework for precise representation of saturation properties and its application to the correlation of pure-fluid vapor pressure, and saturated liquid and saturated vapor densities. Discussions are included regarding the development of each property correlation, evaluations of the proposed framework for use as a correlative tool, and extension of the proposed correlations to simple generalized models.

CHAPTER II

LITERATURE REVIEW

During the course of this work, a review of relevant literature was conducted. No attempt is made here for an extensive discussion of the numerous studies in this area. Only the prediction methods which offer good correlative or predictive capabilities will be addressed. Specifically, literature dealing with the correlation of pure fluid vapor pressure and liquid and vapor densities was surveyed. The theories of corresponding states and critical point scaling law behavior significant to the specific properties considered were also briefly reviewed.

Vapor Pressure Correlations

The literature contains many correlations for prediction of saturation vapor pressure of pure fluids (8,15-19). Most of the existing equations show some basis in the Clapeyron relation which may be expressed as the thermodynamically exact equation:

$$\frac{d(\ln p)}{d(1/T)} = - \frac{\Delta H}{R\Delta Z} \tag{1}$$

Since ΔH and ΔZ are not known explicitly as functions of temperature or pressure, the right side of Equation (1) cannot be integrated analytically. However, assumptions regarding the temperature dependence of ΔH and ΔZ (17) can aid in the development of a vapor pressure equation. Most of the existing equations (8,16,18) simply express lnp as a function of 1/T (or T) as suggested by Equation (1).

Three high precision vapor pressure correlations which are valid over the entire saturated region from the triple point to the critical point were chosen for comparison with the present work. Descriptions the correlations considered for vapor pressure prediction as well as the other saturation properties studied appear in Appendix A. Wagner (16) utilized a statistical method known as "stepwise multiple regression analysis" to determine the most significant terms in an equation which expresses lnp as a polynomial-type function of $(1-T/T_c)$. His resulting equation contains four parameters and correctly exhibits the observed non-analytical behavior of (d^2p/dT^2) at the critical point. Iglesias-Silva and co-workers (17) developed a vapor pressure equation by assuming a temperature dependence for ΔH near the triple point and a functionality for (d^2p/dT^2) near the critical region similar to that suggested by scaling theory. Their resulting set of equations contains three parameters and compares very favorably with other correlations (17). Gomez-Nieto and Thodos (18) developed a set of equations for prediction of vapor pressures of non-polar pure substances. Their correlation is included as a comparison in this work because it represents a nearly generalized correlation requiring only the normal boiling point and critical point properties as input variables.

Liquid Density Correlations

A wide variety of saturated liquid density equations (7,20-26) appear in the literature. Most of these equations express liquid density as a polynomial-type function of $(1-T/T_c)$. Extensive reviews of available models are given elsewhere by several authors (7,20,22).

Based on a survey of the literature cited above, two correlations which are rated highly in the literature (4,21,22) were chosen for comparison with this work, and are described in Appendix A. Both Spencer and Danner's modified Rackett equation (22) and Hankinson and Thomson's correlation (21) provide precise liquid density predictions. The modified Rackett equation contains one substance-specific parameter. Hankinson and Thomson's correlation is a one-parameter equation applicable in the range of $0.25<T_r<0.98$.

Vapor Density Correlations

Several models which are in fairly wide use have been recommended for the prediction of saturated vapor density (4,6,27). However, these methods suffer from the major drawback of requiring both temperature and pressure to calculate vapor density and were not considered for comparison with the proposed model. Instead, an equation which expresses vapor density as a function of temperature only and which is very useful as a data reduction tool was chosen as a comparison for this work.

Several authors (28,29,30) have used equations similar to one used by Goodwin (31) (described in Appendix A) for the correlation of ethane vapor densities. Goodwin's equation contains six parameters and expresses $\ln\rho$ as a polynomial-type function of $(T_c-T)/(T_c-T_t)$ in powers of 1/3 from 1.0 to 2.0. A leading term with an exponent of 0.35 as used by Goodwin (31) for ethane was used for all fluids considered.

The equation provides highly precise vapor density representations. However, the model parameters do not appear to be generalizable and use of this equation as a predictive tool is not promising.

Review of Relevant Theory

As stated above, two of the desired model characteristics are the ability to predict the properties of fluids of widely varying chemical nature and the ability to satisfy established theoretical limiting behavior for the properties considered. Therefore, a review of corresponding states theory and critical point scaling law behavior was conducted. A brief summary of these topics is included to emphasize their significance and influence on this work.

Corresponding States Theory

The principle of corresponding states asserts that physical properties dependent on intermolecular forces are related to the properties at the critical point in the same way for all fluids. In 1939, Pitzer (33) provided a theoretical development based on statistical mechanics of simple molecules which showed that the compressibility factor may be expressed as:

$$Z = Z\left(\frac{\epsilon}{kT}, \frac{V}{N\sigma^3}\right) \tag{2}$$

where ϵ = energy parameter of molecular interaction

σ = molecular separation corresponding to the minimum potential energy of interaction.

k = Boltzmann's constant

By applying the conditions that the first and second derivatives of pressure with respect to volume equal zero at the critical point, Equation (2) can be shown (10) to be equivalent to:

$$Z = Z(T_r,\ v_r) \qquad (3)$$

Pitzer and Curl (13) demonstrated the applicability of this principle to normal fluids by utilizing the acentric factor and extending Equation (3) such that:

$$Z = Z(T_r,\ v_r,\ \omega) \qquad (4)$$

Equation (4) can be further generalized to include as many substance-dependent parameters as necessary:

$$Z = Z(T_r,\ v_r,\ a_1,\ a_2, \ldots a_n) \qquad (5)$$

For a pure fluid in the saturated region, only one variable is required to fix the state of the system, and the compressibility factor (or any other saturation property) can be related to the temperature as:

$$Y = Y(T_r,\ a_1,\ a_2, \ldots a_n) \qquad (6)$$

where Y = any saturation property

The significance of the corresponding states principle is evident from Equation (6) in which a property, Y, can be related to temperature for all substances with the same correlation form. The goal of correlation efforts based on the corresponding states principle then becomes precise representation of saturation properties in terms of reduced variables with simple generalizable relations for the set of structural parameters.

Scaling Law Behavior

Scaling laws are universal relations among the various thermodynamic variables in the immediate vicinity of the critical point as established both by observation and by theoretical models. The relations pertinent to this work can be expressed mathematically as:

$$|Y-Y_c| = A|T-T_c|^B \tag{7}$$

where, Y = vapor pressure or saturated liquid or vapor density

A = a system specific proportionality constant

B = universal critical point exponent common for all fluids

Extensive discussions of universality and critical point exponents are given elsewhere (34-39). Only those results of scaling law theories which are pertinent to this work will be mentioned here.

Scaling theory (16,35) places the following requirement for the limiting behavior of the vapor pressure at the critical point:

$$\lim_{T \to T_c} \frac{(d^2p)}{dT^2} = \infty \tag{8}$$

While scaling theory provides a clear assessment for the value of d^2p/dT^2 at the critical point, little information exists regarding the limiting value of dp/dT. In the study of carbon dioxide, Sengers and Chen (40) have used a value of 1.0 for the critical exponent, B, of Equation (7) to represent vapor pressure data near the critical point.

The critical exponents of the saturated liquid and vapor density curves are identical, and experimentally observed values for these exponents are usually near 0.35 (34). Accurate theoretical predictions for these critical exponents based on three-dimensional Ising-like systems provide a critical exponent for the density curves of 0.325 (37). Such a value for this critical exponent leads to the well accepted criterion that:

$$\lim_{T \to T_c} (d\rho/dT) = \infty \tag{9}$$

$$\lim_{T \to T_c} \frac{(d^2\rho)}{dT^2} = \infty \tag{10}$$

Following the works of Charoensombut-amon and Kobayashi (41) and Gasem and co-workers (82), the usefulness of Equation (7) can be extended to lower temperatures for the saturation densities by coupling the order parameter equation,

$$\phi_+ - \phi_- = \sum_{i=0}^{N} b_i(\tau)^{\beta+i} \tag{11}$$

and the rectilinear diameter equation,

$$(\phi_+ + \phi_-)/2 = \phi_c + a_0(\tau)^{1-\alpha} + \sum_{j=1}^{M} a_j(\tau)^j \tag{12}$$

to develop the following expression for the correlation of coexisting phase densities:

$$\phi_\pm = \phi_c + a_0(\tau)^{1-\alpha} + \sum_{j=1}^{M} a_j(\tau)^j \pm (1/2) \sum_{i=0}^{N} b_i(\tau)^{\beta+i} \tag{13}$$

where $\tau = (T_c - T)/T_c$

ϕ = order parameter (+/- for the liquid and vapor phases, respectively)

α,β = universal scaling-law exponents

N,M = number of expansion terms

a,b = system-specific constants

The leading term (i=0) of Equation (13) is the limiting scaling-law behavior of the order parameter, ϕ, and the subsequent terms in the summation are the Wegner corrections (32) to the limiting scaling behavior. While such an extension is capable of precise representation of phase densities, several parameters are required (a_i's and b_i's) and difficulty in generalizing these parameters deters further development of a predictive correlation based on this type of equation.

CHAPTER III

FRAMEWORK DEVELOPMENT

For a pure fluid in the saturated region, only one fluid property is required to fix the state of the system. Thus, pairs of properties may be related as:

$$dY = (\partial Y/\partial X)_\sigma dX \tag{14}$$

where Y = a saturated fluid property

X = independent correlating variable

and σ indicates a saturation condition.

This relation describes changes in a dependent thermodynamic variable due to changes in an independent variable. For example, one can determine the vapor pressure as a function of temperature by integrating the following equation:

$$dp = (\partial p/\partial T)_\sigma dT \tag{15}$$

For the general case given by Equation (14), applying the boundary condition that,

$$Y = Y_c \text{ at } X = X_c \tag{16}$$

one obtains,

$$Y_c - Y = \int_X^{X_c} (\partial Y/\partial X)_\sigma dX \tag{17}$$

This equation can then be recast as,

$$Y_c - Y = \Theta(X, X_c, \alpha, \alpha_c) \tag{18}$$

where Θ is used to express the integral quantity and α is a set of structural parameters descriptive of the molecular behavior of the fluid of interest. The variable α_c is included as a consequence of the boundary condition that at $X=X_c$, $Y=Y_c$ and $\alpha=\alpha_c$.

To benefit from another boundary condition at the triple point, a second equation can be written as,

$$Y_c - Y_t = \Theta(X_t, X_c, \alpha_t, \alpha_c) \tag{19}$$

Equations (18) and (19) can be combined to produce the following expression for the determination of fluid saturation properties in terms of well defined limits (the critical point and the triple point):

$$\frac{Y_c - Y}{Y_c - Y_t} = \frac{\Theta(X, X_c, \alpha, \alpha_c)}{\Theta(X_t, X_c, \alpha_t, \alpha_c)} \tag{20}$$

To facilitate the correlation of saturation properties, an assumption was made that α could be removed from the right side of Equation (20) by way of the following variable transformation:

$$\frac{Y_c^\alpha - Y^\alpha}{Y_c^\alpha - Y_t^\alpha} = \frac{\Theta(X, X_c)}{\Theta(X_t, X_c)} \tag{21}$$

$$\text{where, } \alpha = \alpha(X, X_t, X_c, \alpha_t, \alpha_c) \tag{22}$$

While this transformation is an assumption, its success is supported by the correlation of vapor pressure (42), liquid density (43) and other saturation properties.

The final step in the development of the general model involves expressing the right side of Equation (21) as a function of only one variable defined as,

$$\epsilon = \frac{X_c - X}{X_c - X_t} \qquad (23)$$

so that Equations (21) and (22) may be written as,

$$\frac{Y_c^\alpha - Y^\alpha}{Y_c^\alpha - Y_t^\alpha} = \Theta(\epsilon) \qquad (24)$$

$$\text{where} \quad \alpha = \alpha(\epsilon, \alpha_t, \alpha_c) \qquad (25)$$

In this way, the structural dependence of fluid behavior is now well referenced between the limiting behaviors at the critical point (which exhibits elements of universality) and the triple point (which is highly substance specific).

The framework given by Equations (24) and (25) is identical to that which has been used in previous studies at Oklahoma State University to correlate physical properties, where Y included such properties as T_b, T_c, p_c, and ω (1,2,44) for normal paraffins, and Θ was expressed as:

$$\Theta = \exp(-C_1 X) \qquad (26)$$

where C_1 = correlation constant

X = carbon number

$\alpha = C_2$ (a second correlation constant)

Such a definition has lead to precise correlations for these physical properties of normal paraffins with reasonable extrapolation capability, allowing for predictions of properties for the heavier members of this homologous series (for which experimental data are unavailable).

CHAPTER IV

DATA REDUCTION PROCEDURE

Various strategies have been suggested for the reduction of vapor pressure data (16,45) with each trying to reflect the level of confidence placed in the different measurements considered. Although highly precise and internally-consistent data are available, special attention is still recommended when dealing with pressures below 1 kPa, since such measurements tend to have relatively larger percentage errors (45).

Ideally, a weighted least squares objective function is desirable for all of the properties studied, since this permits each data point to be assessed an appropriate weight to reflect the uncertainty associated with the measurement. For the systems considered in this study, however, excellent overall fits were obtained using the relative error objective function given below:

$$SS = \Sigma\{(Y_{calc} - Y_{exp})/Y_{exp}\}^2 \tag{27}$$

where Y_{exp} = experimental saturation property

Y_{calc} = calculated saturation property

The present model includes both the triple point (Y_t) and critical point (Y_c) saturation properties as input variables. To avoid the uncertainties in these two end points having a disproportionate effect on the overall quality of fit, both end point saturation property values were treated as adjustable parameters and were evaluated as part of the overall regression, but were constrained to differ from the literature values by no more than the average relative error of the data points in the regression. The end point saturation properties used as input parameters in the evaluations of the literature models were treated in the same manner.

The procedure used in the development of all correlations given here consisted of the following. First, a database was compiled containing highly reliable data for the development of each correlation. Where possible, experimental data were used to avoid the influence of other workers' smoothing functions on the development of these correlations. Second, this database was used to test the ability of the proposed model to correlate the saturation properties of widely varying chemical species using as many substance-specific parameters as required, and comparisons were made with the selected literature models. Finally, generalized models for vapor pressure and liquid density were developed based on this database and checked against data on other substances in a second database which, in general, consisted of lesser quality data. A preliminary generalized correlation was developed for prediction of vapor densities, but it has not been checked against additional data.

A Marquart (46) nonlinear regression procedure was employed in the calculations. Definitions of the statistics used in this study are given in the Nomenclature.

Database Employed

Appendix B gives a complete list of the physical properties and the ranges and sources of all data used in the development stage of each correlation and in the development of each model generalization. Also included in Appendix B are the ranges and sources of all data used to check the generalized models for vapor pressure and liquid density. A comprehensive description of all cases studied during the course of this work is given in the following chapter.

CHAPTER V

VAPOR PRESSURE MODEL

Model Development

The development of the vapor pressure correlation involves determination of the functions for Θ and α of Equations (24) and (25). Appendix B details the database employed in this study to determine the forms of the Θ and α functions. Table B.1 gives the critical and triple point properties used and Table B.2 presents the sources and ranges of data used.

A variety of functional forms for Θ and α were evaluated in the course of this work. As a result (based on regressions of the data set in Table B.2), the following equations are proposed to describe the temperature dependence of Θ and α:

$$\Theta = \frac{1 - A^{\epsilon^{B}}}{1 - A} \tag{28}$$

and

$$\frac{\alpha_c - \alpha}{\alpha_c - \alpha_t} = \frac{\epsilon + C\epsilon^2}{1 + C} \tag{29}$$

where,

$$\epsilon = \frac{T_c - T}{T_c - T_t} \tag{30}$$

A,B,C = correlation constants

α_c = the limiting value of α at the critical point temperature.

α_t = the limiting value of α at the triple point temperature.

Thus, recasting Equation (24),

$$Y = \{Y_c^{\alpha} - (Y_c^{\alpha} - Y_t^{\alpha})\Theta\}^{(1/\alpha)} \qquad (31)$$

and applying Equations (28), (29), and (30) as definitions for Θ, α, and ϵ results in the proposed model for the correlation of pure-fluid vapor pressure, where Y becomes p.

Figure 1 illustrates the variation of the reduced vapor pressure with reduced temperature for a number of compounds with different degrees of acentricity and polarity. The figure indicates that the reduced vapor pressure depends upon two separate factors -- the temperature and the chemical nature of the substance.

Using the proposed framework given by Equation (31), the variations in the vapor pressure with temperature and chemical structure are presented by two simple functions both of which are temperature dependent. The first, given by Equation (28), presents the effect of reduced temperature on the correlating function, Θ, and the second, as shown in Figure 2, depicts the variation of the scaling exponent, α, with reduced temperature, ϵ. As given, the proposed correlation:

(a) provides for a universal representation for the scaled-then-reduced pressure, Θ, in terms of the reduced temperature, ϵ, and

(b) accounts for variation due to the chemical structure through the limiting values of the scaling exponent (α_c and α_t).

(Note that in the context of this work, a scaled variable is one raised

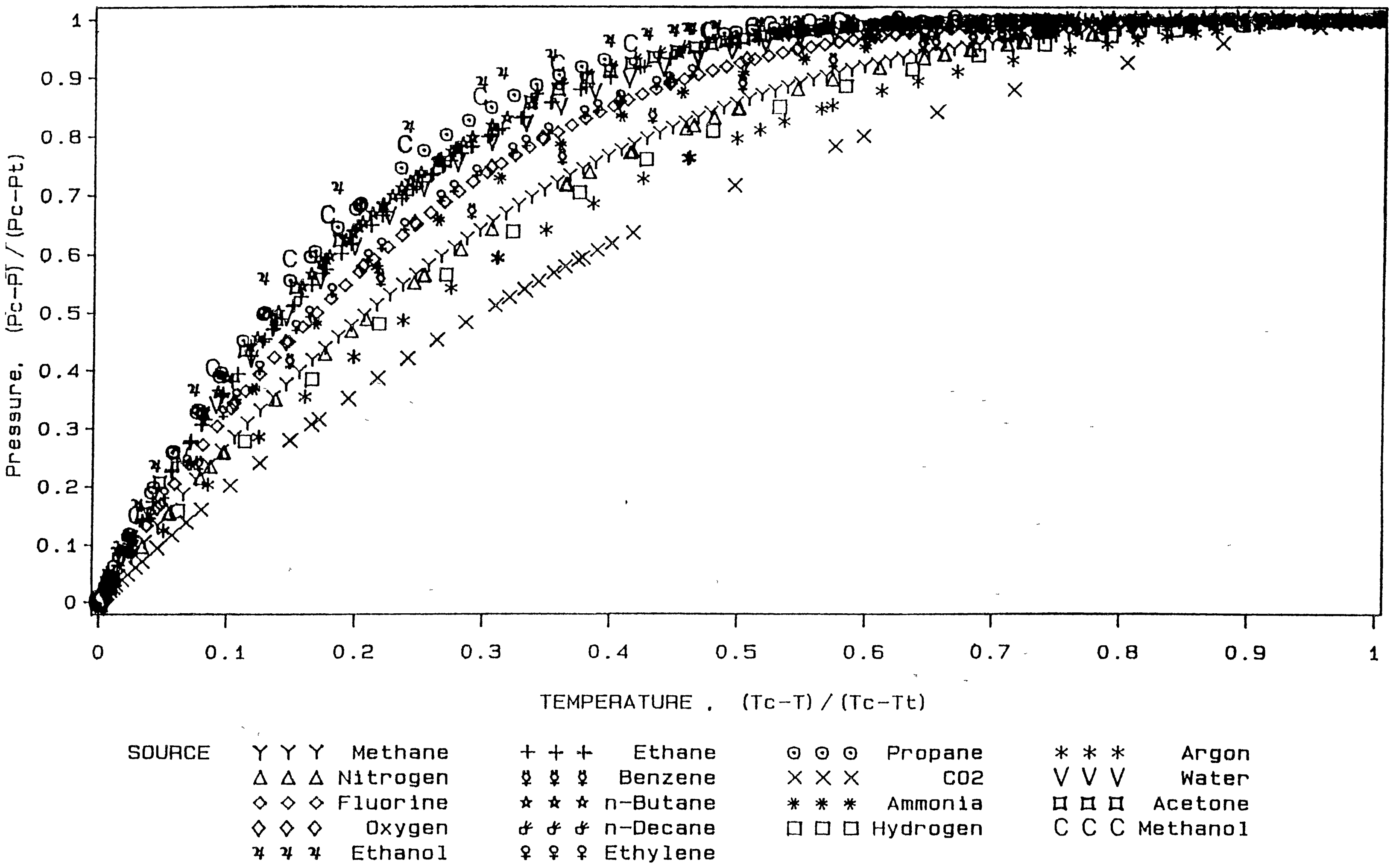

Figure 1. Vapor Pressure Variation with Temperature

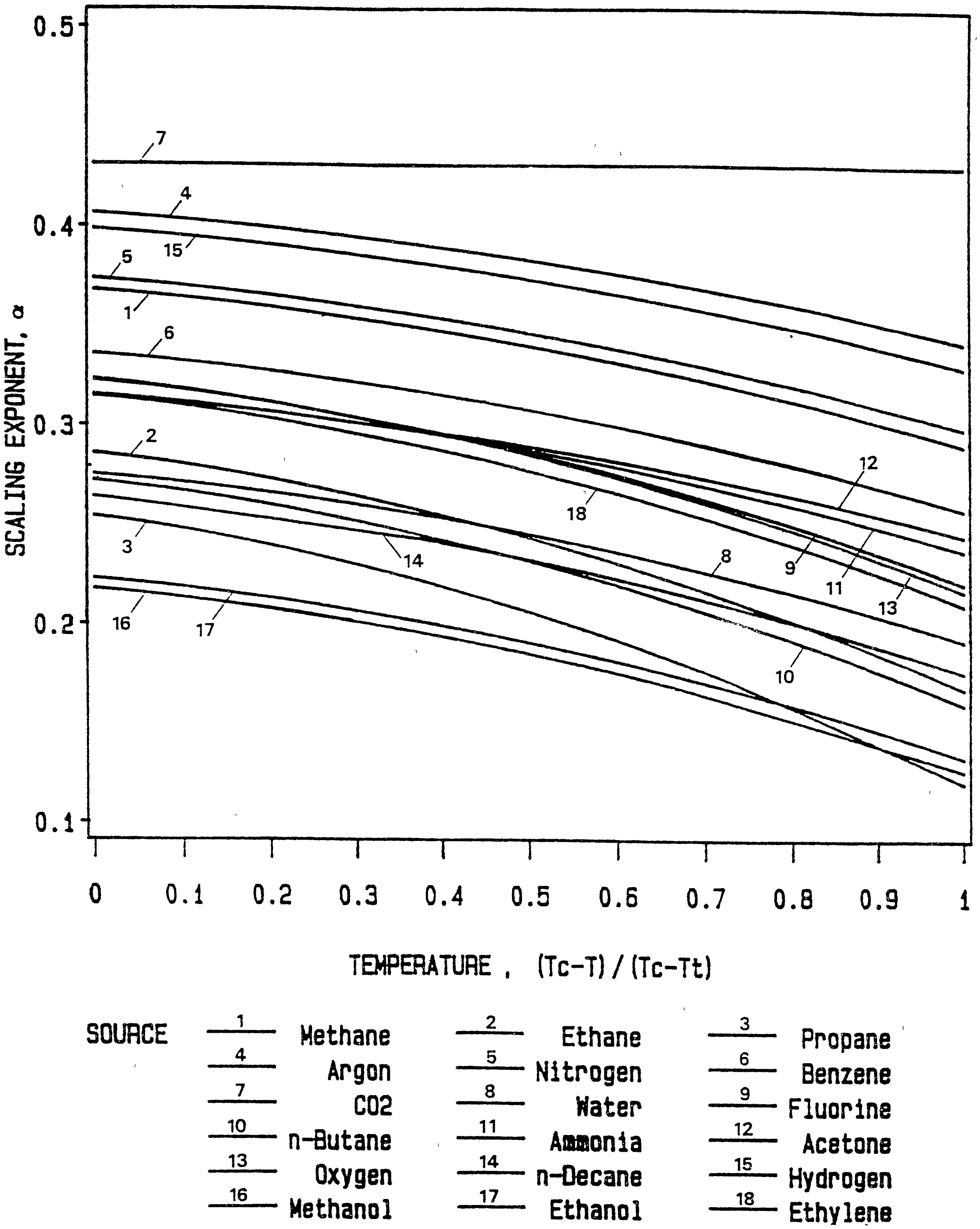

Figure 2. Effect of Temperature on the Vapor Pressure Scaling Exponent

to a power, e.g., Y^{α}, and a reduced variable is one divided by the critical property, Y/Y_c, or the adjusted critical, $(Y_c-Y)/(Y_c-Y_t)$.)

Further evidence for the ability of α_c and α_t to account for effects of variation in the chemical species is given by Figure 3, where values of α_c and α_t show a strong correlation with the reduced triple point temperature, T_{rt}, which is highly substance dependent. Figure 3 also shows predicted values of α_c and α_t which are described later in this chapter.

Criteria of Evaluation

One of the basic requirements for a useful saturation property correlation is accurate representation of experimental data (within their uncertainty) over the complete saturation range. Figures 4 and 5 present error plots for ethane and nitrogen in which B, α_c, and α_t in Equations (28) and (29) are treated as system specific parameters. The quality of fit produced by the proposed vapor pressure correlation is excellent and compares favorably with the results obtained from the Wagner (16) and Iglesias et. al. (17) equations.

Several criteria for the development of vapor pressure correlations have been proposed over the years by Riedel (19), Waring (8), Ambrose (47) and Chase (15). While such criteria have evolved from experimental and phenomenological observations, most lack a sound theoretical basis. Accordingly, careful examination of the validity for such criteria is required prior to their adoption.

Scaling theory (16,35,36) places the following requirement for the limiting behavior of the vapor pressure at the critical point

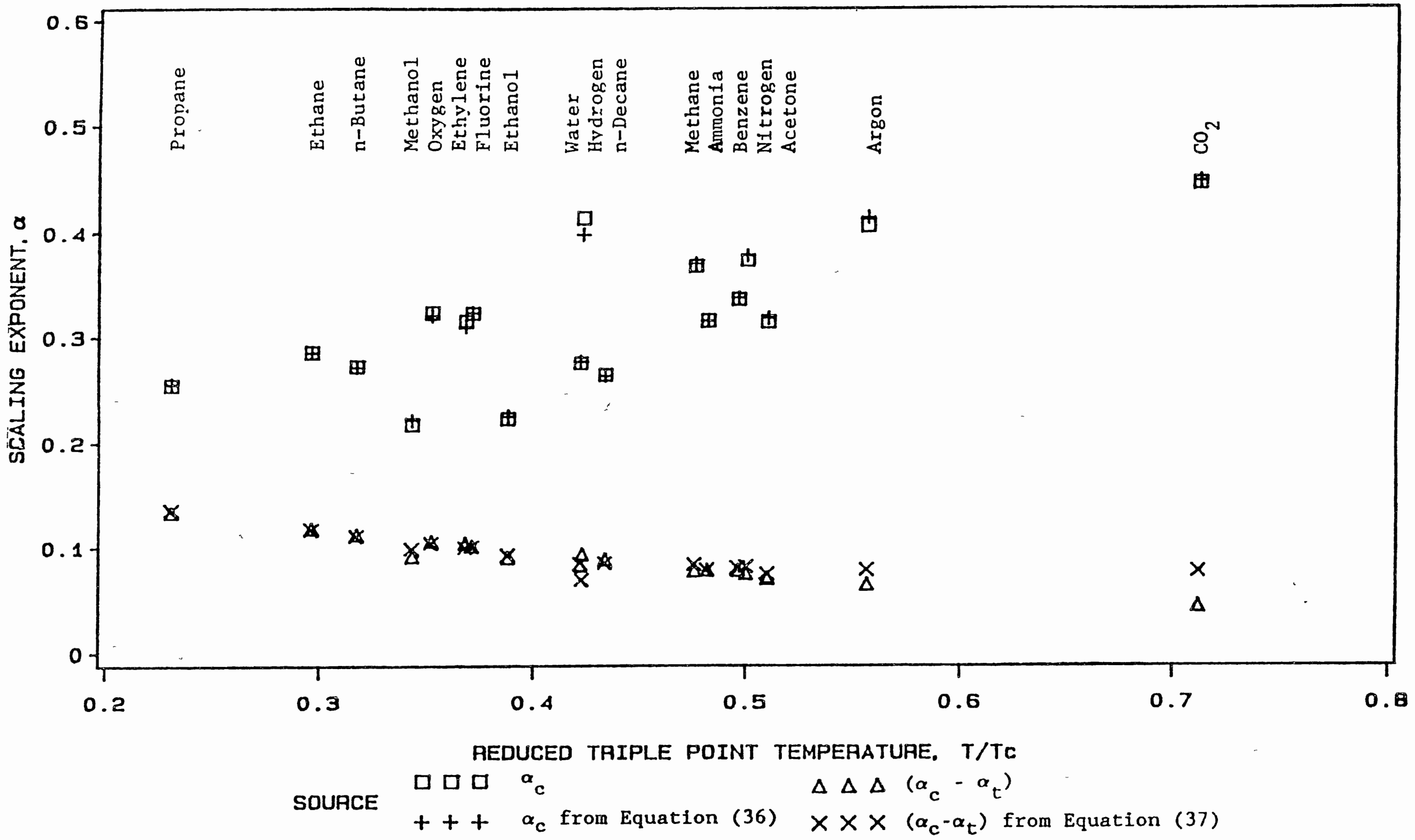

Figure 3. Effect of Reduced Triple Point Temperature on Limiting Values of Vapor Pressure Scaling Exponents

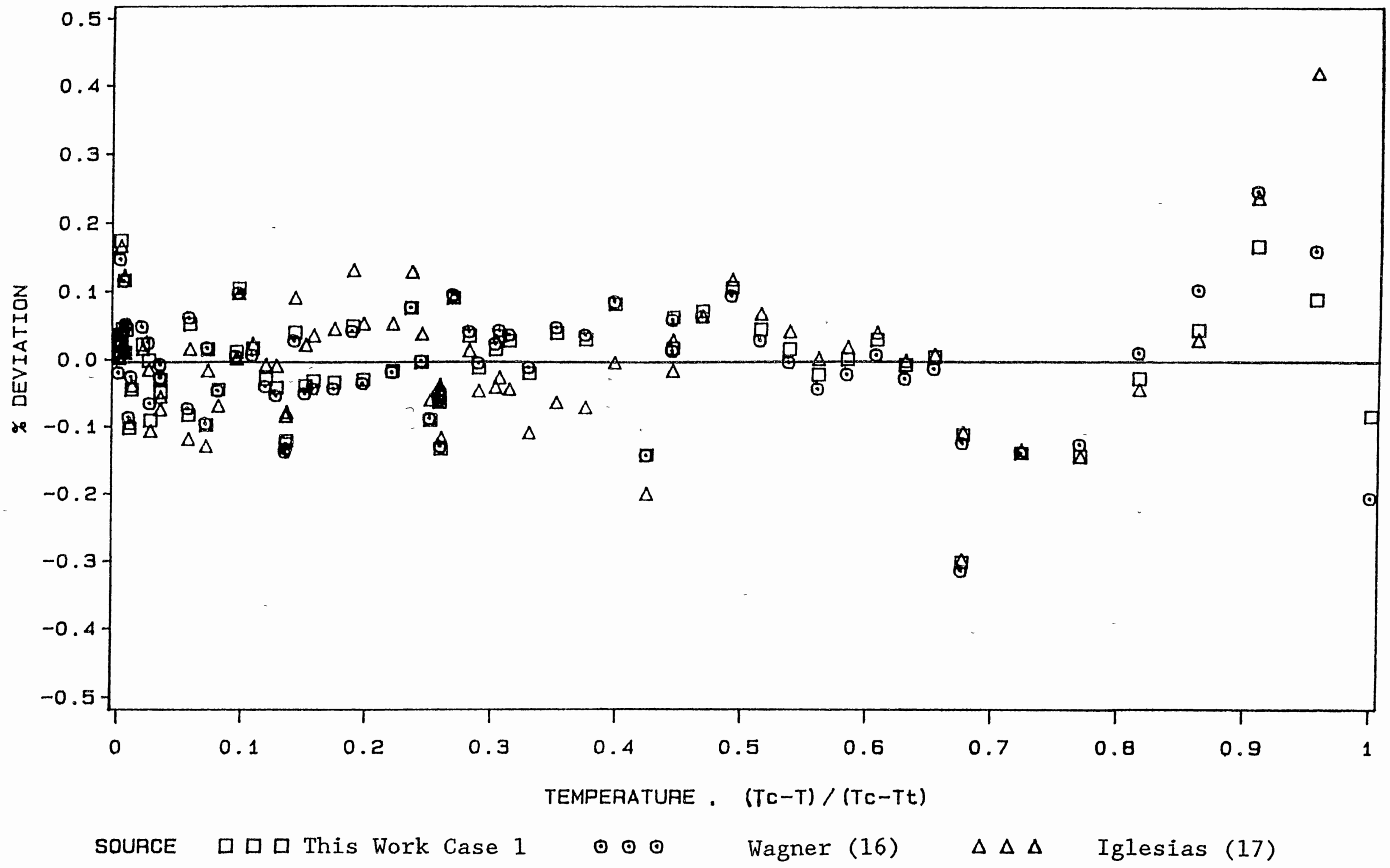

Figure 4. Comparison of Ethane Vapor Pressure Representations

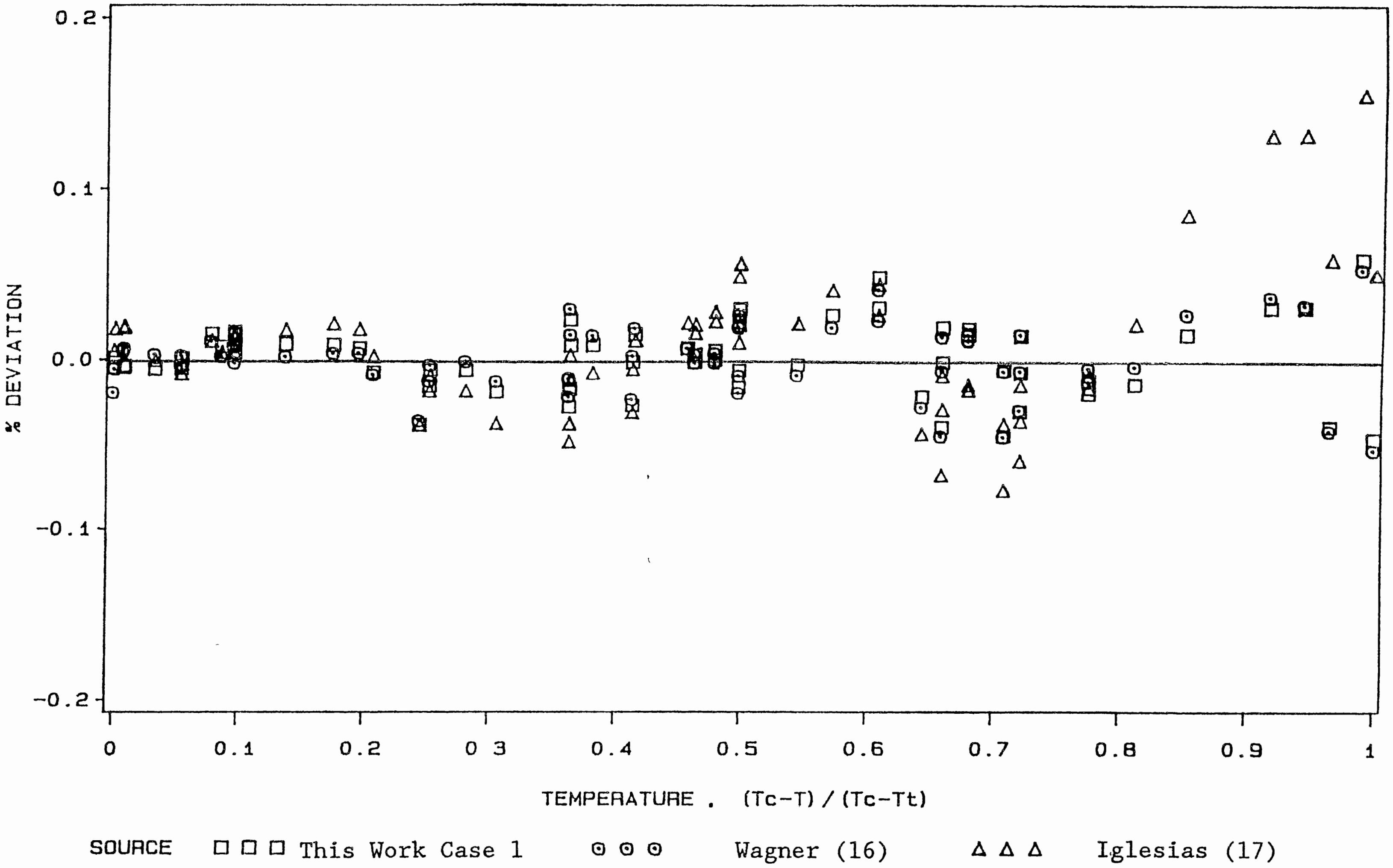

Figure 5. Comparison of Nitrogen Vapor Pressure Representations

$$\lim_{T \to T_c} \left(\frac{d^2p}{dT^2}\right) = \infty \tag{32}$$

The proposed correlation satisfies this scaling law behavior. However, it is at odds with the Riedel-Plank criterion, which requires a zero value for $d\alpha/dT$ ($\alpha = (T/p)(dp/dT)$) at the critical point. Similarly, Wagner (16) concluded that the Riedel-Plank criterion is not suitable for the fluids he considered. He stated that it cannot be entirely excluded that both $d\alpha/dT$ and d^2p/dT^2 would become infinite as $T \to T_c$.

While scaling theory provides a clear assessment for the value of d^2p/dT^2 at the critical point, little information exists regarding the limiting value of dp/dT. An expression for $(dp/dT)_c$ for the proposed correlation is as follows:

$$(dp/dT)_{\epsilon \to 0} = \left(\frac{p_c^{(1-\alpha_c)}}{\alpha_c}\right)(p_c^{\alpha_c} - p_t^{\alpha_c})\left(\frac{1}{T_c - T_t}\right)\left(\frac{B \ln A}{A-1}\right)\epsilon^{B-1} \tag{33}$$

Thus, the limiting value of dp/dT at the critical point depends on the value of B. For the fluids considered in this study, a value of $B<1$ was found to be optimum. This implies that dp/dT at the critical point is infinite. During the course of the evaluation of the proposed correlation, it was found that setting $B=1$ or $B>1$, to force $(dp/dT)_c$ to be either zero or finite, consistently resulted in a worsened fit of the experimental data.

Based on the proposed correlation, the approach of dp/dT to infinity as the critical point is approached is rather slow, since the value of dp/dT remains finite at $\epsilon=10^{-10}$. Actually, the value of dp/dT at $\epsilon=10^{-10}$ for ethane was found to be comparable to that obtained using the Wagner equation, which produces a finite limiting value for $(dp/dT)_c$.

The Waring criterion (8) requires a minimum to exist in the $\Delta H/\Delta Z$ vs T_r plot at a reduced temperature of about 0.8 to 0.85. This criterion, in turn, would satisfy Thodos'(18) observation for the existence of an inflection point in lnp curve with (1/T), since

$$\frac{\Delta H}{\Delta Z} = -R \frac{d(\ln p)}{d(1/T)} \tag{34}$$

Figure 6 presents the variation of $\Delta H/\Delta Z$ with reduced temperature for ethane as given by the proposed correlation which is clearly in agreement with Waring's criterion.

The discussion thus far has dealt with criteria that apply at temperatures above the normal boiling point. For lower temperatures, $T<0.6T_c$, comparison of the calculated $\Delta H/\Delta Z$ values with those based on experimental measurements offers a reasonable check on the applicability of a given correlation at low temperatures. Such agreement between the two quantities signifies that the rate of change of pressure with respect to temperature is in accordance with the Clausius-Clapeyron equation expressed by Equation (34). As shown in Figure 6, a favorable comparison exists between the calculated $\Delta H/\Delta Z$ and those based on experimental measurements (deviations within 0.5%).

Model Evaluation

As indicated by Equations 28-30, the proposed correlation contains five parameters, A, B, C, α_c, and α_t. Studies have indicated, however, that good precision is retained when some of these parameters are

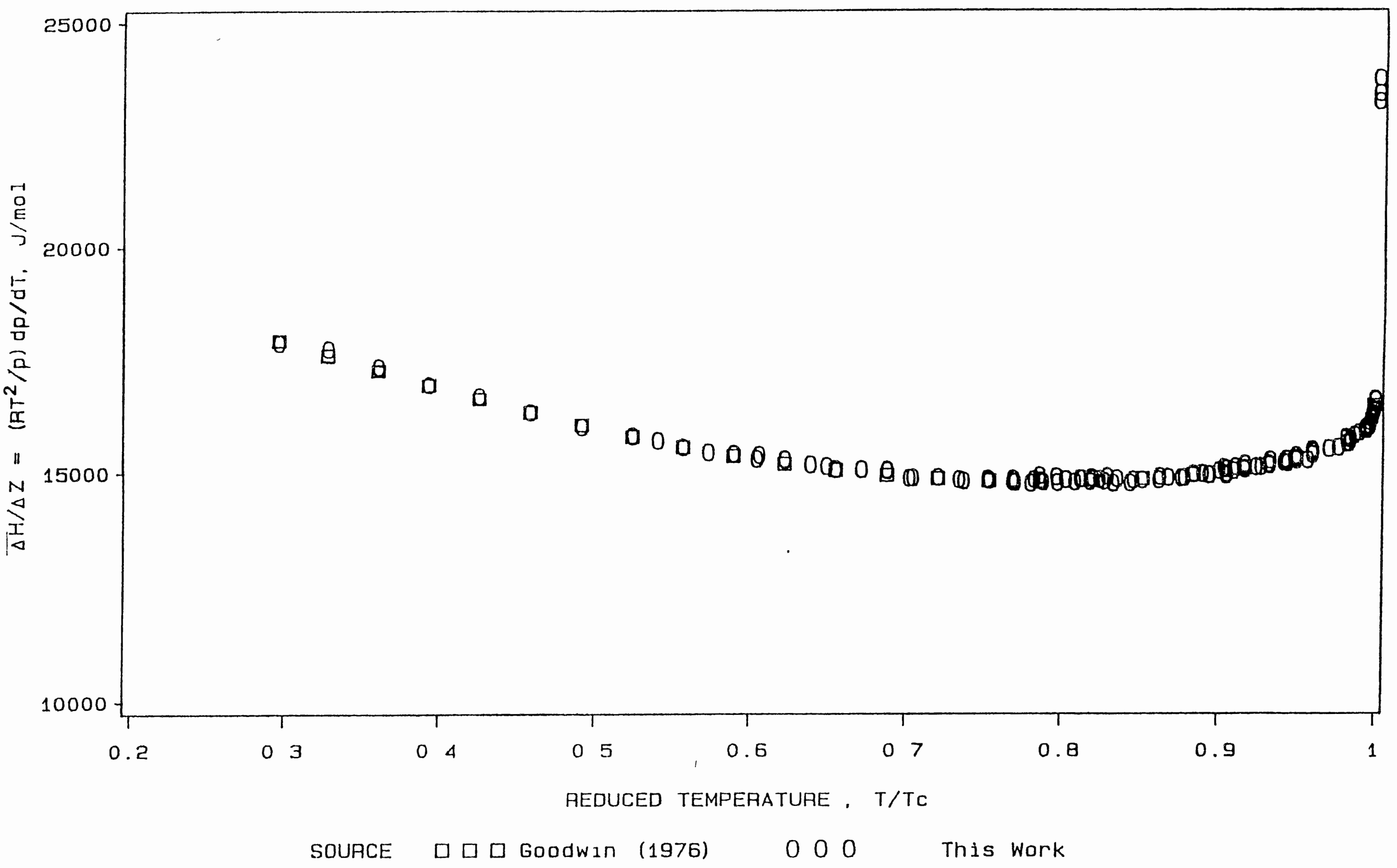

Figure 6. Ethane dp/dT Variation with Temperature

treated as universal constants. Simple values for two of the parameters (A = 2/3, C = 4/3) were determined by regression of the data set in Table B.2. Five cases were studied during the evaluation of the vapor pressure model and are described in Table I.

The evaluation of the first two cases is presented in Table II and the regressed parameters for these cases are reported in Table C.1 of Appendix C. In the first case (Case 1), A and C are treated as universal constants, and α_c, α_t, and B are substance-specific. In Case 2, α_c and α_t are treated as substance-specific and B is common.

Comparison of the results for the two cases indicates that for the most accurate representation of experimental data, the flexibility offered by a three constant equation is desirable and leads to precise representation of the experimental data for each of the various fluids considered (RMSE = 0.021, and %AAD = 0.057). In comparison, the results of Case 2, a two-constant model, show only a minor deterioration in the overall quality of the fit (RMSE = 0.022, and %AAD = 0.067). Possibly more significant from a data correlation point of view is the distribution of error for a given fluid where, as expected, Case 1 is better.

Table II also presents a comparison of the present work with two correlations which are rated favorably in the literature (17,45). Contrasting the results obtained for Cases 1 and 2 to those of Wagner (a four-constant equation) (16) and Iglesias et al. (a three-constant equation) (17) indicates a general equivalence in performance (%AAD within 0.1%), with both Case 1 and Wagner's equation giving slightly better fits (%AAD of about 0.05%).

Assessment of the overall value of the present correlation, based

TABLE I

DESCRIPTIONS OF ALL CASES STUDIED IN THE PRESENT WORK

Case	Description
	Vapor Pressure Correlation (Equations 28-30)
1	Three-parameter model. A=2/3, C=4/3 B, α_c, $\Delta\alpha$ regressed as substance-specific parameters.
2	Two-parameter model. A=2/3, B=0.985, C=4/3 α_c, $\Delta\alpha$ regressed as substance-specific parameters.
3	One-parameter model. A=2/3, B=0.985, C=4/3, $\Delta\alpha$ from Equation (37). α_c regressed as a single substance-specific parameter.
4	Generalized model from triple point to critical point. A=2/3, B=0.985, C=4/3, α_c from Equation (36), $\Delta\alpha$ from Equation (37).
5	Generalized model from normal boiling point to critical point. A=2/3, B=0.985, C=4/3, α_c and $\Delta\alpha$ from Equations (36) and (37) with T_t and P_t replaced by T_b and 1.01325 bar.
	Liquid Density Correlation (Equations 38-40)
6	Three-parameter model. B=0.325 A, α_c, $\Delta\alpha$ regressed as substance-specific parameters.
7	Two-parameter model. A=4/3, B=0.325 α_c, $\Delta\alpha$ regressed as substance-specific parameters.
8	One-parameter model. A=1.07068, B=0.325, $\Delta\alpha$ from Equation (44). α_c regressed as a single substance-specific parameter.
9	Generalized model from triple point to critical point. A=1.07068, B=0.325, α_c from Equation (45), $\Delta\alpha$ from Equation (44).

TABLE I (Continued)

Case	Description
10	Generalized model from normal boiling point to critical point. $A=1.07068$, $B=0.325$, α_c and $\Delta\alpha$ from Equations (45) and (44) with T_t and ρ_t replaced with T_b and ρ_b.
	Vapor Density Correlation (Equations 46-48)
11	Four-parameter model. $A_2=0.5$, $B_2=1.325$, $C=0.7$ A_1, B_1, α_c, $\Delta\alpha$ regressed as substance-specific parameters.
12	Three-parameter model. $A_1=4.8$, $A_2=0.5$, $B_2=1.325$, $C=0.7$ B_1, α_c, $\Delta\alpha$ regressed as substance-specific parameters.
13	Two-parameter model. $A_1=4.8$, $A_2=0.5$, $B_1=0.325$, $B_2=1.325$, $C=0.7$ α_c and $\Delta\alpha$ regressed as substance-specific parameters.
14	One-parameter model. $A_1=3.11$, $A_2=0.6$, $B_1=0.325$, $B_2=1.269$, $C=0.6$, $\Delta\alpha$ from Equation (51). α_c regressed as a single substance-specific parameter.
15	Generalized model from triple point to critical point. $A_1=3.11$, $A_2=0.6$, $B_1=0.325$, $B_2=1.269$, $C=0.6$, $\Delta\alpha$ from Equation (51), α_c from Equation (50).

TABLE II

VAPOR PRESSURE MODEL EVALUATION

	This Work				Literature			
	Case 1		Case 2		Wagner (16)		Iglesias(17)	
	RMS, bar	%AAD	RMS, bar	%AAD	RMS, bar	%AAD	RMS, bar	%AAD
Methane	0.005	0.015	0.005	0.016	0.005	0.015	0.010	0.053
Ethane	0.017	0.054	0.021	0.068	0.017	0.056	0.018	0.065
Propane	0.015	0.067	0.012	0.066	0.010	0.039	0.010	0.063
Argon	0.003	0.017	0.006	0.025	0.002	0.015	0.005	0.024
Nitrogen	0.002	0.016	0.005	0.024	0.002	0.015	0.003	0.030
Benzene	0.006	0.014	0.008	0.019	0.004	0.014	0.014	0.051
CO_2	0.004	0.007	0.004	0.007	0.008	0.013	0.032	0.043
Water	0.051	0.043	0.034	0.047	0.022	0.022	0.033	0.047
Fluorine	0.007	0.069	0.006	0.072	0.002	0.051	0.010	0.079
n-Butane	0.037	0.176	0.030	0.184	0.026	0.131	0.032	0.172
Ammonia	0.028	0.031	0.054	0.056	0.026	0.011	0.047	0.048
Acetone	0.017	0.054	0.024	0.055	0.018	0.061	0.016	0.048
Oxygen	0.018	0.084	0.018	0.106	0.006	0.032	0.020	0.127
n-Decane	0.001	0.057	0.002	0.061	0.001	0.054	0.002	0.142
Hydrogen	0.002	0.056	0.012	0.105	0.005	0.071	0.012	0.196
Methanol	0.040	0.092	0.064	0.169	0.027	0.065	0.037	0.088
Ethanol	0.057	0.154	0.060	0.251	0.038	0.077	0.072	0.157
Ethylene	0.006	0.066	0.009	0.073	0.006	0.063	0.019	0.171
Overall	0.021	0.057	0.022	0.067	0.014	0.045	0.023	0.081

Case 1: A=2/3,C=4/3
Case 2: A=2/3,B=0.985,C=4/3

on the number of regressed parameters and the potential for simple generalizations, shows it to be it highly viable and perhaps superior to others evaluated. Extension of the proposed model to a completely generalized form based on the compounds given in Table B.2 follows.

Model Generalization

The ultimate goal of any correlation development is a generalized model that can provide precise and reliable *a priori* predictions for all systems including those on which no experimental data are available. The ability of Case 2 (in which only α_c and $(\alpha_c-\alpha_t)$ are treated as substance-specific parameters) to provide highly precise predictions for a wide range of chemical species has already been demonstrated. This, along with the observed systematic dependence of α_c and $(\alpha_c-\alpha_t)$ with reduced triple-point temperature, as shown in Figure 3, suggests the possibility for the development of a generalized model based on the generalization of α_c and $(\alpha_c-\alpha_t)$. The development of a generalized equation for α_c begins with the assumption that α_c can be expressed as,

$$\alpha_c = f_i + f_s + \sum_j \Psi_j \tag{35}$$

in which f_i represents the basic functional dependence of α_c on the reduced initial point temperature (preferably the triple-point temperature) and f_s represents the observed variation of α_c with Z_c for simple fluids. The Ψ_j's represent other correction terms included to account for variations of α_c with known physical properties. Based on close inspection of Figure 3, three Ψ_j corrections were included: the first to account for variation in Z_c from a simple fluid Z_c value of

0.29, the second to account for variations in ω, and the third to account for observed variations in the ratio of ω/Z_c. Based on regressions of the data set given in Table B.2, the following form was selected for α_c:

$$\alpha_c = C_1 T_{rt}^{C_2} + C_3 Z_c^{C_4} + [C_3^{(Z_c-0.29)} + C_5^{\omega} + C_6^{(3\omega-\omega/Z_c)} - 3.0] \qquad (36)$$

Similar arguments lead to the following form for $(\alpha_c\text{-}\alpha_t)$:

$$(\alpha_c\text{-}\alpha_t) = C_1 T_{rt}^{C_2} + C_3 Z_c^{C_4} + (C_1\text{-}1) T_{rt}^{C_4} + [C_3^{(Z_c-0.29)} - 1.0]C_7 \qquad (37)$$

The constants C_1-C_7 were determined from regressions of the data set given in Table B.2 and are reported in Appendix C in Table C.2. In order to test the generality of the relations given in Equations (36) and (37), a database of 29 additional substances was compiled as given in Table B.3 of Appendix B. The vapor pressures of all substances shown in Tables B.2 and B.3 were then predicted using Equations (36) and (37). Results of three cases based on the generalized equation are given in Table III. In Case 3, $(\alpha_c\text{-}\alpha_t)$ is determined from Equation (37) and α_c is a regressed substance-specific parameter, and in Case 4 both α_c and $(\alpha_c\text{-}\alpha_t)$ are calculated from Equations (36) and (37). Case 5 shows the results of using the normal boiling point as the lower vapor pressure point (T_{rb} is substituted for T_{rt}) along with Equations (36) and (37) to predict vapor pressures between the normal boiling point and the critical point.

The results of Case 3 demonstrate the advantages of a one-parameter model using the proposed framework. The quality of the fit obtained (%AAD = 0.58%) combined with the convenience of only one

TABLE III

EVALUATION OF GENERALIZED VAPOR PRESSURE MODEL

	This Work						Literature	
	Case 3		Case 4		Case 5		Gomez (18)	
Substance	RMS, bar	%AAD	RMS, bar	%AAD	RMS, bar	%AAD	RMS, bar	%AAD
Methane	0.049	0.209	0.017	0.346	0.043	0.335	0.021	0.118
Ethane	0.020	0.084	0.018	0.083	0.121	0.499	0.027	0.152
Propane	0.058	0.241	0.044	0.362	0.116	0.478	0.028	0.592
Argon	0.067	0.264	0.064	0.342	0.063	0.323	0.053	0.242
Nitrogen	0.030	0.188	0.030	0.282	0.026	0.363	0.044	0.354
Benzene	0.029	0.072	0.015	0.211	0.060	0.403	0.022	0.541
Carbon Dioxide	0.074	0.187	0.096	0.302	0.096	0.302	0.030	0.065
Water	0.150	0.134	0.207	0.590	1.365	2.487	3.594	10.21
Fluorine	0.005	0.066	0.030	0.776	0.099	0.444	0.043	0.553
n-Butane	0.047	0.265	0.036	0.371	0.157	0.968	0.023	1.461
Ammonia	0.048	0.060	0.091	0.206	0.195	0.474	0.712	3.378
Acetone	0.035	0.195	0.024	0.274	0.084	0.388	0.034	2.517
Oxygen	0.017	0.141	0.057	1.094	0.045	0.337	0.037	1.441
n-Decane	0.053	0.274	0.002	0.800	0.008	0.378	0.006	1.227
Hydrogen	0.040	0.667	0.032	0.800	0.008	0.161	0.041	3.142
Methanol	0.138	0.765	0.063	0.628	0.742	3.063	0.173	2.866
Ethanol	0.301	1.631	0.257	1.799	0.096	0.291	0.427	2.320
Ethylene	0.096	0.388	0.075	1.510	0.039	0.248	0.055	2.186
Neon	0.053	0.392	0.068	0.602	0.052	0.428	0.108	2.117
Propylene	0.010	0.309	0.061	2.948	0.061	0.384	0.028	1.057
o-Xylene	0.079	0.419	0.144	1.431	0.150	0.823	0.015	0.494
Acetic Acid	0.294	1.188	0.515	7.027	0.902	5.222	0.453	9.248
Propanol	0.444	2.090	0.177	3.463	0.138	1.053	0.421	9.240
tert-Butanol	0.188	1.338	0.062	1.438	0.104	0.974	0.272	5.648
Hydrogen Cyanide	0.182	0.945	0.397	4.080	0.360	2.196	0.271	3.317
Toluene	0.066	0.301	0.104	0.978	0.123	0.635	0.017	0.321
Methyl Isobutyrate	0.354	2.269	0.187	2.375	0.116	1.910	0.244	3.218
Acetylene	0.393	0.859	0.589	1.613	0.587	1.608	0.395	1.716
Bromine	0.184	0.578	0.416	1.828	0.215	0.252	0.152	1.007
Methyl Chloride	0.411	1.792	0.691	2.798	0.767	1.132	0.665	2.314
Chlorine	0.080	0.255	0.067	0.533	0.067	0.496	0.076	0.570
Carbon Tetrachloride	0.162	1.755	0.182	2.345	0.242	0.784	0.170	3.245
Deuterium	0.053	0.470	0.078	1.218	0.053	0.347	0.116	2.721
Deuterium Oxide	0.078	0.214	0.032	0.440	1.166	1.725	2.597	14.68
n-Heptane	0.067	1.312	0.026	2.500	0.129	0.901	0.005	0.986
Refrigerant 11	0.023	0.141	0.060	1.073	0.130	0.563	0.025	0.469
Refrigerant 12	0.024	0.090	0.093	1.454	0.136	0.604	0.013	0.239
Refrigerant 13	0.272	1.524	0.140	2.954	0.034	0.413	0.174	12.94
Refrigerant 13B1	0.025	0.130	0.044	0.724	0.037	0.288	0.074	0.664
Refrigerant 22	0.170	0.869	0.019	1.408	0.115	0.519	0.010	1.280

TABLE III (Continued)

	This Work						Literature	
	Case 3		Case 4		Case 5		Gomez (18)	
Substance	RMS, bar	%AAD	RMS, bar	%AAD	RMS, bar	%AAD	RMS, bar	%AAD
Refrigerant 23	0.064	0.172	0.150	1.351	0.174	0.603	0.097	1.433
Refrigerant 113	0.016	0.147	0.019	0.215	0.063	0.522	0.032	0.444
Refrigerant 114	0.066	0.528	0.029	1.606	0.060	0.504	0.065	0.764
Refrigerant 115	0.043	0.296	0.106	1.093	0.058	0.365	0.050	0.284
Refrigerant 500	0.021	0.063	0.112	1.612	0.085	0.888	0.889	21.79
Sulfur Dioxide	0.080	0.842	0.082	0.939	0.138	0.535	0.110	1.610
Xenon	0.062	0.282	0.057	0.576	0.059	0.502	0.117	0.388
Overall	0.111	0.583	0.125	1.349	0.206	0.832	0.277	2.927

substance-specific input variable makes this an attractive approach in dealing with complex molecular species for which completely generalized predictions are inadequate.

Table III also presents a comparison of Case 4 with the predictions of the Gomez-Thodos model (18) which requires the normal boiling point, T_b, as an input variable. As shown in Table III, Case 4 and Gomez-Thodos (18) are essentially equivalent for normal fluids with Case 4 providing considerably better predictions for polar fluids such as water. For the various fluids included in this comparison, the proposed framework appears to give better predictions as indicated by the overall %AAD of 1.35%, which is about half the value obtained from the Gomez-Thodos model.

In the event that the triple point conditions are not available as input parameters, the normal boiling point may be used as the lower vapor pressure point (where T_{rb} is substituted for T_{rt}) along with Equations (36) and (37) to predict vapor pressures between the normal boiling point and the critical point with reasonable accuracy. Results using the normal boiling point as the lower end point are shown as Case 5 in Table III. Case 5 indicates that for most fluids considered use of the normal boiling point as the lower vapor pressure point results in only minor changes in the quality of vapor pressure predictions (%AAD of 1.35% and 0.83% for Cases 4 and 5, respectively). These results may be attributed to the fact that vapor pressure measurements below atmospheric pressure contain larger uncertainties.

CHAPTER VI

LIQUID DENSITY MODEL

Model Development

The development of the liquid density model follows the same procedure as for the vapor pressure model. The forms for the Θ and α functions of Equations (24) and (25) were determined from regressions of the saturated liquid density data given in Tables B.4 and B.5 of Appendix B. The same definition for Θ was chosen as for the correlation of vapor pressures,

$$\Theta = \frac{1 - A^{\epsilon^{B}}}{1 - A} \tag{38}$$

along with the following form for α,

$$\frac{\alpha_c - \alpha}{\alpha_c - \alpha_t} = \frac{1 - A^{\epsilon}}{1 - A} \tag{39}$$

where

$$\epsilon = \frac{T_c - T}{T_c - T_t} \tag{40}$$

A = correlation constant

B = theoretical scaling law exponent value of 0.325

α_c = the limiting value of α at the critical point temperature.

α_t = the limiting value of α at the triple point temperature.

Thus, recasting Equation (24),

$$Y = \{Y_c^{\alpha} - (Y_c^{\alpha} - Y_t^{\alpha})\Theta\}^{(1/\alpha)} \qquad (41)$$

and applying Equations (38), (39), and (40) as definitions for Θ, α, and ϵ results in the proposed model for the correlation of pure-fluid saturated liquid densities, where Y becomes ρ_L.

Figure 7 illustrates the variation of the reduced densities with reduced temperature, ϵ, for some of the compounds listed in Table B.5. The figure indicates that the reduced density depends on both the temperature and the chemical structure of the substance.

As with the vapor pressure model, the proposed correlation given by Equation (41) represents the variations in the liquid density with temperature and chemical structure with the two simple functions, Θ and α, both of which are temperature dependent. The first, as given by Equation (38), represents the effect of reduced temperature on the correlating function, Θ, and the second, as shown in Figure 8, depicts the variation of the scaling exponent, α, with the reduced temperature, ϵ. Again, the ability of α_c and α_t to account for effects of variation in the chemical species is demonstrated by Figure 9, where values of α_c and α_t show a strong correlation with the reduced triple-point temperature, T_{rt}, which is highly substance-dependent.

Criteria of Evaluation

One of the desired features of the saturation property correlation is accurate representation of experimental data (within their uncertainty) over the complete saturation range. Figures 10 and 11

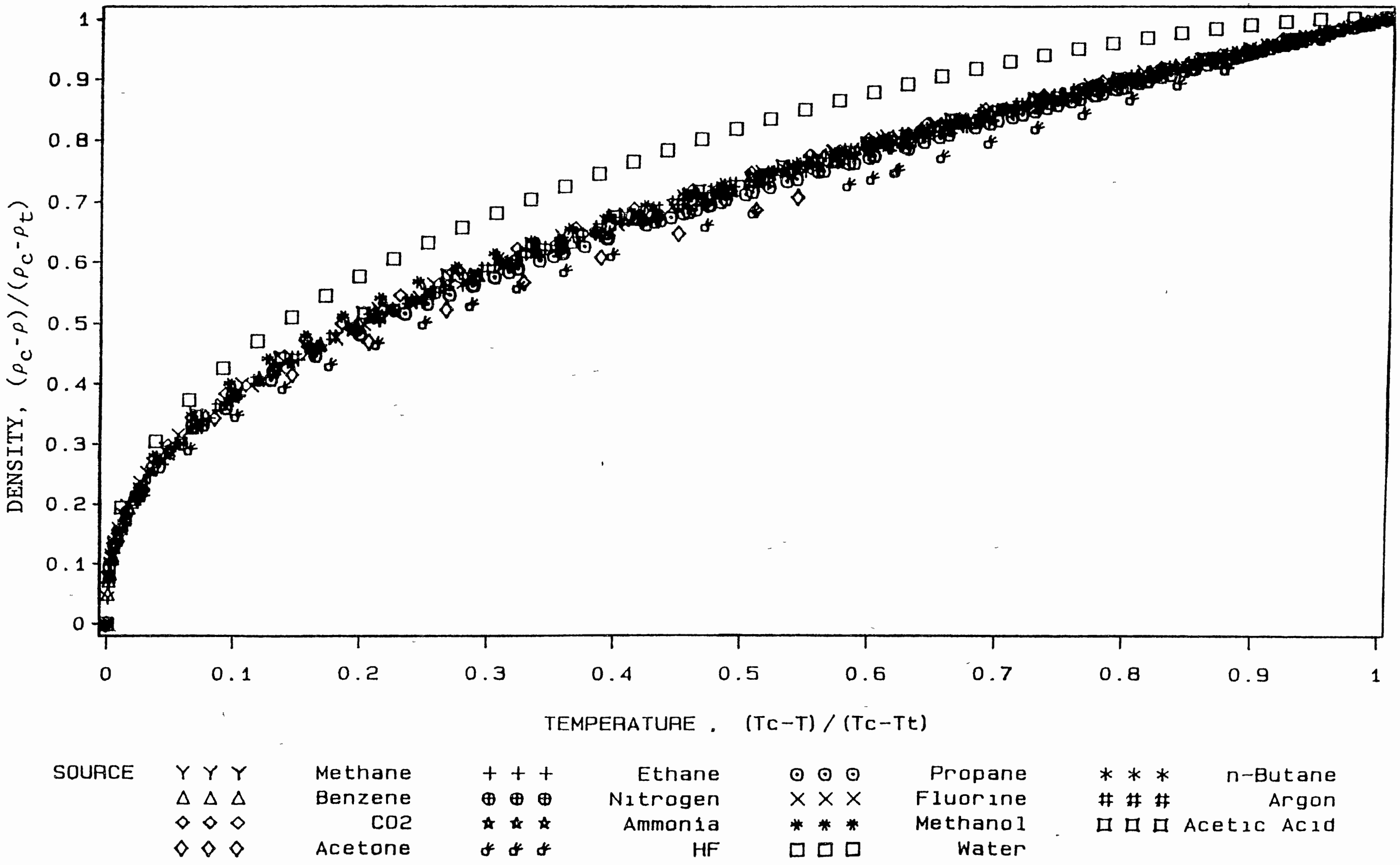

Figure 7. Saturated Liquid Density Variation with Temperature

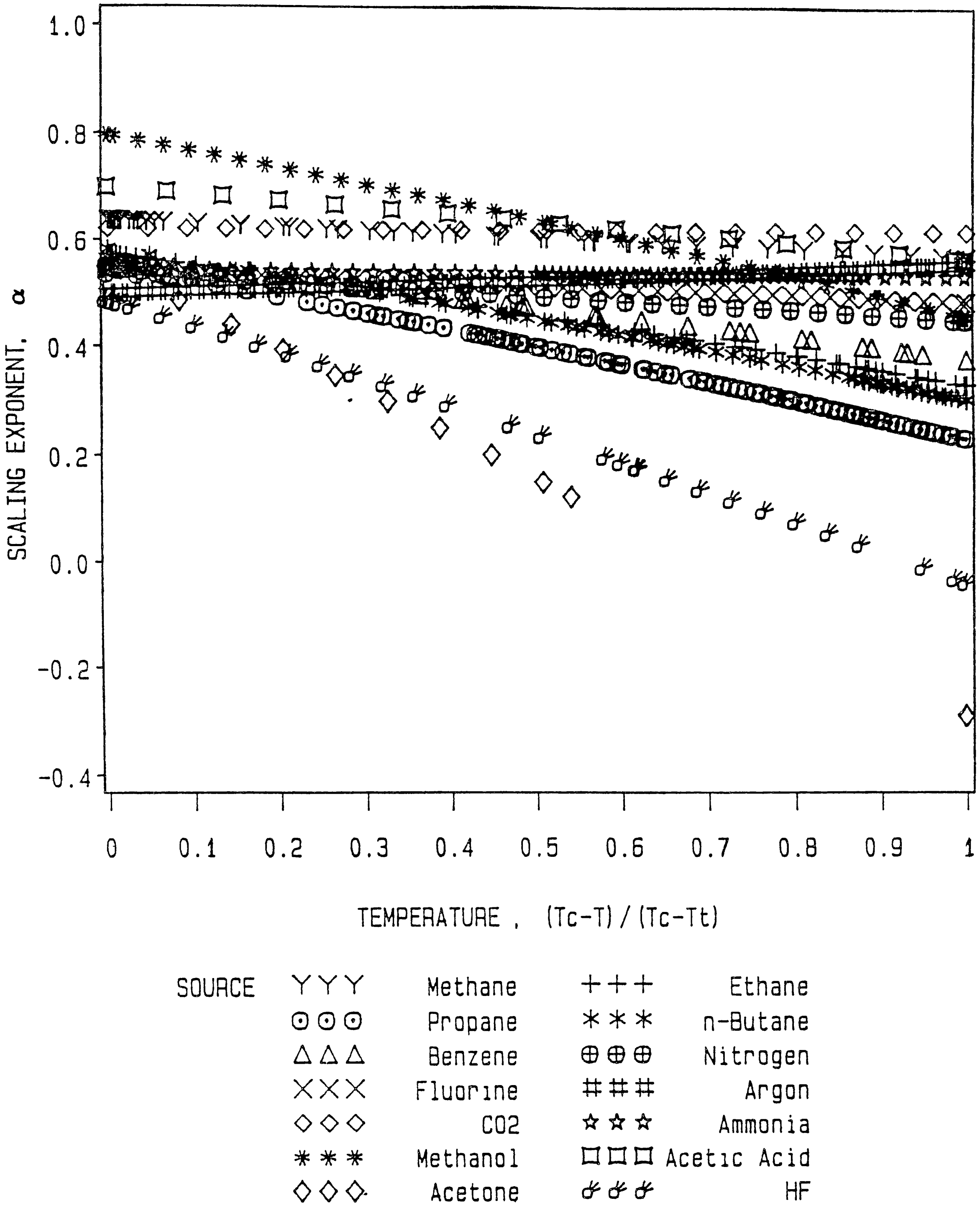

Figure 8. Effect of Temperature on the Saturated Liquid Density Scaling Exponent

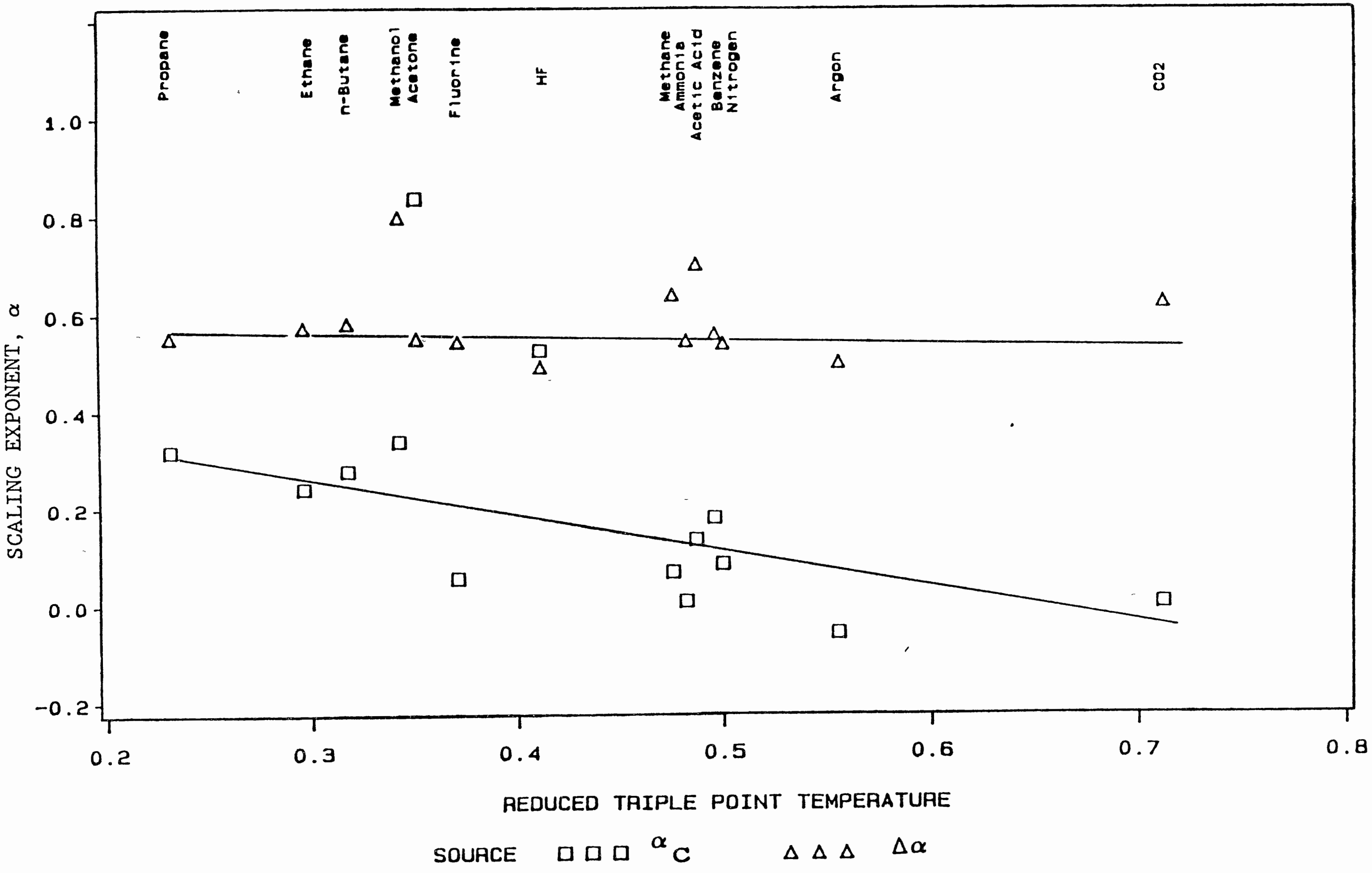

Figure 9. Effect of Reduced Triple Point Temperature on Limiting Values of the Saturated Liquid Density Scaling Exponents

illustrate the ability of the proposed liquid density correlation, as shown for ethane. Figure 10 shows the results for three cases (Cases 6-8) described in Table I. While regression of the three model parameters (A, α_c, α_t) of the proposed liquid density correlation certainly fits the experimental data within their precision, the quality of fit produced by regressing only one model parameter remains excellent. Figure 11 shows that Case 8 (one substance-specific parameter, α_c) compares favorably with the results obtained from the Hankinson-Thomson (21) and the modified Rackett (22) equations within the range of application deemed most appropriate for these two correlations ($0.25 < T_r < 0.95$).

As discussed earlier, scaling-law behavior provides a constraint on the behavior of density near the critical point (34). In the immediate vicinity of the critical point, coexisting densities should be described by Equation (7). Accordingly, to satisfy the stated requirement of obeying the theoretical limits of behavior at the critical point, the proposed model must, in an expanded form, yield a leading term with the appropriate scaling-law exponent (35). In an expanded form the present model can be written as,

$$\rho = \rho_c + a_1\epsilon^B + a_2\epsilon^{2B} + \ldots \tag{42}$$

Thus, the current model has a leading term similar to that of Equation (7). The currently accepted value for the density critical point scaling exponent, as predicted by three-dimensional Ising-like systems, is 0.325 (35). This is the value adopted for B in Equation (38).

Comparison of Equation (42) with Equation (13) discussed earlier suggests that the proposed model produces a functional form similar to

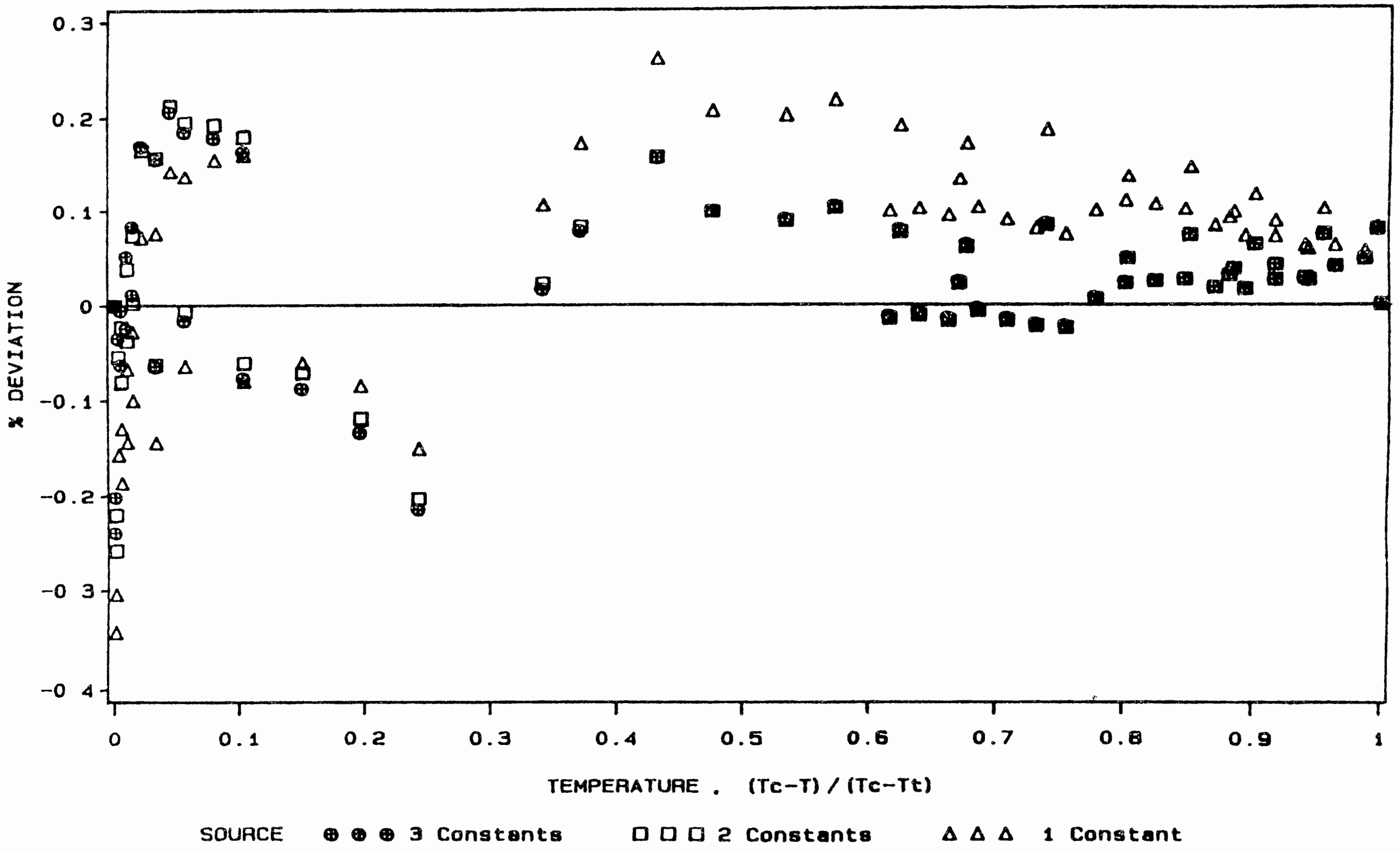

Figure 10. Comparison of Ethane Liquid Density Representations

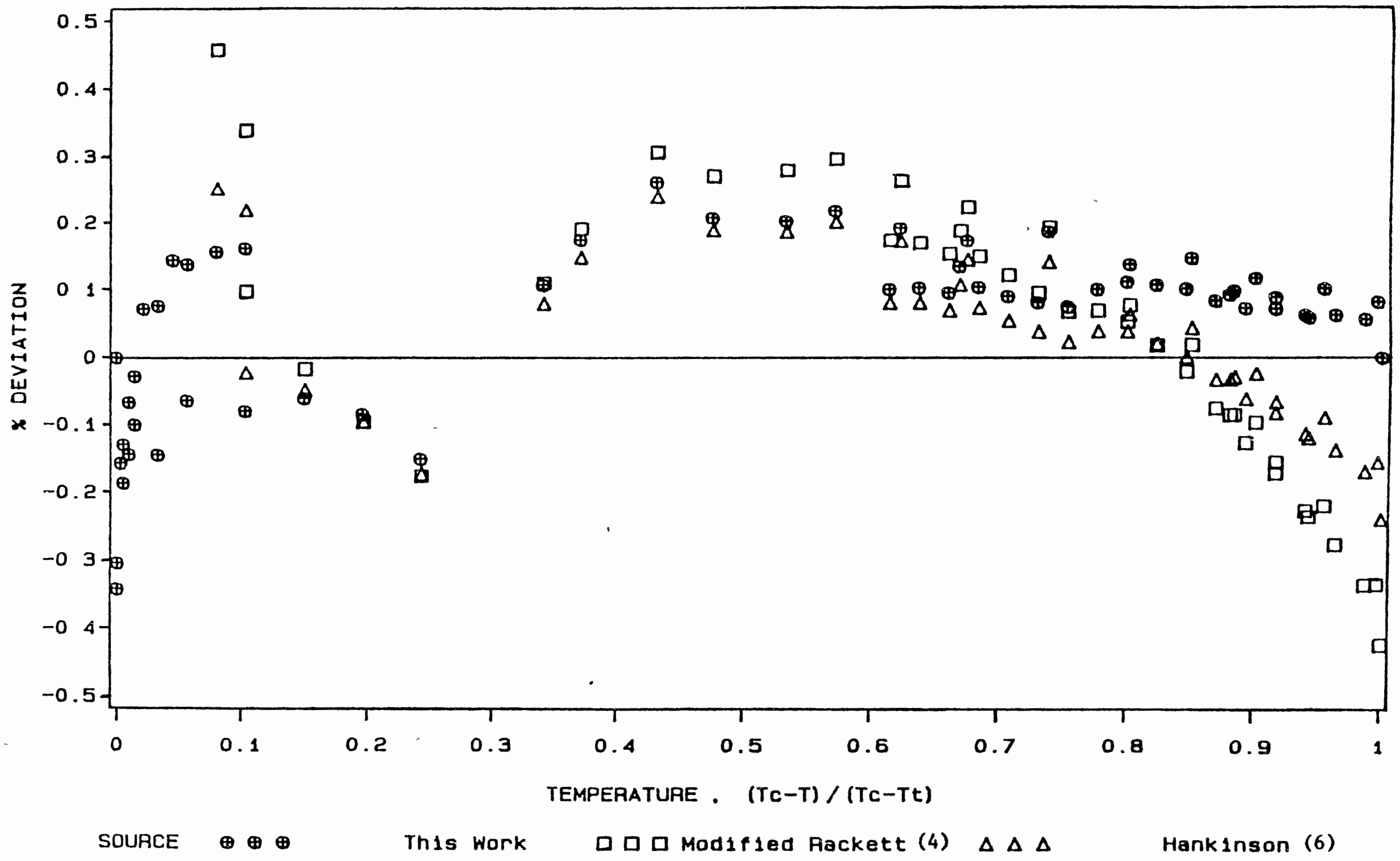

Figure 11. Comparison of Ethane Liquid Density Representations with Literature Models

that obtained from extended scaling theory with the added advantages of being a closed-form equation and containing parameters that appear descriptive of molecular structure.

Model Evaluation

As indicated by Equations (38) and (39), the proposed correlation contains four parameters, A, B, α_c, and α_t. The present studies, however, have indicated that a good level of precision may be obtained by treating some of the parameters as universal constants that apply to all fluids, and, as already stated, B was set equal to the theoretical scaling-law value of 0.325 for all cases considered.

Five specific cases were studied as described in Table I and results of the first three cases (Cases 6-8) are presented in Table IV. In Case 6, the three model parameters (A, α_c, α_t) are treated as substance-specific parameters. In Case 7, only α_c and α_t are treated as substance-specific, and in Case 8, (α_c - α_t) comes from a generalized equation discussed in the next section and only α_c is treated as substance-specific. Values for the regressed parameters of these cases are listed in Table C.3 of Appendix C.

Comparison of Cases 6-8 indicate that for the most accurate representation of experimental data, the flexibility offered by a three constant equation is desirable and leads to precise representation of the experimental data for the various fluids considered (RMSE = 0.96 Kg/m^3 and %AAD = 0.10). By comparison, the results of Case 7 (a two constant model) show only minor deterioration in the overall quality of the fit (RMSE = 1.07 Kg/m^3 and %AAD = 0.11). Possibly more significant from a correlation point of view, however, is the distribution of error

TABLE IV

LIQUID DENSITY MODEL EVALUATION

	This Work						Literature			
	Case 6		Case 7		Case 8		Rackett (22)		Hankinson(21)	
Substance	RMSE, Kg/m^3	%AAD	RMSE, Kg/m^3	%AAD	RMSE, Kg/m^3	%AAD	RMSE, Kg/m^3	%AAD	RMSE, Kg/m^3	%AAD
Methane	0.639	0.159	0.682	0.180	0.641	0.159	0.369	0.086	0.585	0.127
Ethane	0.707	0.080	0.713	0.081	0.715	0.085	1.327	0.192	0.954	0.121
Propane	0.364	0.044	0.374	0.046	0.422	0.055	1.993	0.250	1.292	0.157
n-Butane	0.296	0.040	0.296	0.040	0.508	0.068	1.373	0.179	0.763	0.100
Benzene	1.197	0.208	1.236	0.215	1.459	0.234	1.380	0.138	1.948	0.193
Nitrogen	0.968	0.127	0.949	0.125	0.941	0.127	2.832	0.364	1.892	0.239
Fluorine	0.310	0.022	0.409	0.030	0.987	0.068	2.337	0.134	0.764	0.040
Argon	1.240	0.085	1.386	0.101	1.410	0.105	3.792	0.282	1.642	0.116
CO_2	0.405	0.037	0.458	0.040	0.416	0.036	2.565	0.209	2.851	0.236
Ammonia	0.179	0.026	0.199	0.030	1.021	0.145	1.302	0.183	3.974	0.560
Water	1.999	0.184	2.474	0.196	11.99	1.177	31.67	3.069	23.73	2.103
Hydrogen	0.174	0.229	0.191	0.253	0.441	0.610	1.071	1.421	1.507	1.981
Methanol	2.232	0.286	2.486	0.328	2.278	0.311	19.37	2.383	15.80	1.909
Propylene	0.391	0.056	0.379	0.055	0.591	0.071	4.297	0.539	3.850	0.479
Neon	0.952	0.082	1.048	0.093	2.015	0.183	3.506	0.287	5.082	0.380
Oxygen	0.537	0.048	0.559	0.050	0.556	0.050	3.076	0.225	1.248	0.085
Freon 12	1.526	0.095	1.597	0.100	2.388	0.141	6.425	0.261	5.308	0.219
Acetic Acid	0.713	0.065	1.457	0.130	1.354	0.137	19.93	2.029	7.408	0.731
Acetone	1.370	0.174	1.409	0.180	5.874	0.691	9.223	1.088	12.05	0.778
n-Decane	0.911	0.121	0.895	0.117	2.099	0.212	2.444	0.259	2.761	0.373
Cyclohexane	0.912	0.101	0.909	0.101	1.819	0.218	2.083	0.244	2.038	0.244
Hydrogen Fluoride	1.202	0.119	1.192	0.118	1.535	0.153	28.27	3.009	33.00	2.825
Overall	0.959	0.099	1.071	0.108	2.828	0.189	10.24	0.629	9.041	0.531

Case 6: B=0.325
Case 7: A=4/3, B=0.325
Case 8 A=1.07068, B=0.325, $\Delta\alpha$ from Equation (44)

for a given fluid, where (as expected) Case 6 produces better error distribution as shown in Figure 10 for ethane.

Extension of the proposed liquid density correlation to a generalized model through the development of generalized equations for α_c and $(\alpha_c - \alpha_t)$ follows.

Model Generalization

Development of a generalized model for prediction of saturated liquid densities is done through the development of generalized equations for $\Delta\alpha$ and α_c. As shown in Figure 9, a strong relation exists between the regressed values for $\Delta\alpha$ and α_c and T_{rt}. A linear relation was established between $\Delta\alpha$ and T_{rt} for simple fluids (those with Z_c values near 0.29):

$$\Delta\alpha = C_1 + C_2 T_{rt} \tag{43}$$

The variations exhibited by other fluids were then accounted for by an exponential relation such that:

$$\Delta\alpha = C_1 + C_2 T_{rt}^{(C_3 + C_4 Z_c)} \tag{44}$$

While the form of Equation (44) is merely a depiction of the observed variation of $\Delta\alpha$ with T_{rt} for simple fluids, the exponential term was selected to account for deviation from simple fluid behavior through the value of Z_c. As shown in Case 8 (in which α_c is a single substance-specific parameter and $\Delta\alpha$ is from Equation (44)) in Table IV, the overall quality of fit remains reasonable (RMSE = 2.83 kg/m^3, %AAD = 0.19). However, individual fluids such as water show significant deviations.

The one-parameter model as represented by Case 8 compares very favorably with the one-parameter models of the modified Rackett equation (22) and the Hankinson-Thomson correlation (21). As shown by the results given in Table IV, using the same database and constrained to their recommended range of application, both the modified Rackett correlation (RMSE = 10.24 kg/m^3, %AAD = 0.63) and the Hankinson-Thomson correlation (RMSE = 9.04 kg/m^3, %AAD = 0.53) produce more than twice the error obtained from the present correlation. Perhaps more importantly, the new model covers the full saturation range, while the literature models were evaluated only over the range of $0.25<T_r<0.95$. Case 9 of Table V presents the results of a completely generalized model in which the following form for α_c (developed on the similar arguments given above for $\Delta\alpha$) along with the above relation for $\Delta\alpha$ was used:

$$\alpha_c = C_5 + C_6 T_{rt}^{(C_7 + C_8\omega)} \tag{45}$$

Values for the constants C_1 through C_8 were determined from regressions based on data for the first 14 compounds listed in Table B.5 and are listed in Table C.4 of Appendix C. The remaining eight compounds in Table B.5 were used along with the compounds listed in Table B.6 as checks on the generalized model and the errors shown in Table V are based on the parameters in Table C.4. As shown in Table V, the only fluid which shows a significant deviation is water with a %AAD of 6.23%. This may be attributed to the strong hydrogen-bonding nature of water.

As with the generalized model for vapor pressure, reasonable

TABLE V

RESULTS OF THE GENERALIZED LIQUID DENSITY MODEL

	Case 9		Case 10	
Substance	RMSE, Kg/m^3	%AAD	RMSE, Kg/m^3	%AAD
Methane	1.84	0.63	1.70	0.61
Ethane	1.01	0.16	2.40	0.61
Propane	0.51	0.37	1.68	0.34
n-Butane	0.76	0.10	1.61	0.27
Benzene	2.38	0.35	1.72	0.29
Nitrogen	2.57	0.31	2.69	0.34
Fluorine	1.39	0.10	0.43	0.03
Argon	5.04	0.43	4.71	0.40
Carbon Dioxide	3.54	0.35	3.54	0.35
Ammonia	2.81	0.41	1.10	0.16
Water	54.87	6.23	23.48	2.84
Hydrogen	0.90	1.19	0.45	0.64
Methanol	2.74	0.34	27.95	4.18
Propylene	2.70	0.44	0.94	0.17
Neon	3.32	2.97	2.05	0.19
Oxygen	2.52	0.23	0.61	0.05
Refrigerant 12	3.88	0.25	4.12	0.29
Acetic Acid	6.36	0.68	7.99	0.92
Acetone	12.67	1.53	3.00	0.33
n-Decane	3.19	0.51	23.51	4.93
Cyclohexane	3.57	0.41	4.24	0.45
Hydrogen Fluoride	2.03	0.23	2.63	0.35
Acetylene	7.04	1.37	7.04	1.37
Bromine	25.65	0.94	21.96	0.78
Methyl Chloride	9.35	0.87	12.25	1.21
Chlorine	11.92	0.83	7.25	0.52
Carbon Tetrafluoride	1.98	0.12	2.15	0.13
iso-Butane	1.00	0.16	2.28	0.42
n-Heptane	3.30	0.49	1.43	0.21
Refrigerant 13	15.05	1.05	13.97	0.96
Refrigerant 22	25.44	1.93	13.31	1.05
Sulfur Dioxide	17.03	1.12	18.55	1.37
Toluene	3.92	0.53	3.02	0.44
Xenon	12.70	0.28	30.61	1.17
Overall	7.50	0.82	7.54	0.83

predictions are obtained (RMSE = 7.54 kg/m^3, %AAD = 0.83) by using the normal boiling point as the lower liquid density value along with Equations (44) and (45) discussed above. The results of this case (Case 10) are presented in Table V for all of the compounds considered.

CHAPTER VII

VAPOR DENSITY MODEL

Model Development

The development of the vapor density model follows the same procedure as for the vapor pressure and liquid density models. The forms for the Θ and α functions of Equations (24) and (25) were determined from regressions of the saturated vapor density data given in Tables B.7 and B.8 of Appendix B. Similar forms for Θ and α were chosen as for the correlation of liquid density,

$$\Theta = \frac{1 - A_1\epsilon^{B_1} - A_2\epsilon^{B_2}}{1 - A_1 - A_2} \tag{46}$$

$$\frac{\alpha_c - \alpha}{\alpha_c - \alpha_t} = \frac{1 - A_1\epsilon^{C} - A_2\epsilon}{1 - A_1 - A_2} \tag{47}$$

where

$$\epsilon = \frac{T_c - T}{T_c - T_t} \tag{48}$$

A_1, A_2, B_1, B_2, C = correlation constants

α_c = the limiting value of α at the critical point temperature.

α_t = the limiting value of α at the triple point temperature.

Thus, recasting Equation (24),

$$Y = \{Y_c^{\alpha} - (Y_c^{\alpha} - Y_t^{\alpha})\Theta\}^{(1/\alpha)} \tag{49}$$

and applying Equations (46), (47), and (48) as definitions for Θ, α, and ϵ results in the proposed model for the correlation of pure-fluid saturated vapor densities, where Y becomes ρ_V.

Figure 12 illustrates the variation of the reduced vapor density with reduced temperature, ϵ, for the compounds listed in Table B.7. The figure indicates that the reduced density depends on both the temperature and the chemical structure of the substance.

As with the vapor pressure and liquid density models, the proposed correlation given by Equation (49) represents the variations in the vapor density with temperature and chemical structure with two functions, Θ and α, both of which are temperature dependent. The first, as given by Equation (46), represents the effect of reduced temperature on the correlating function, Θ, and the second, as shown in Figure 13, depicts the variation of the scaling exponent, α, with the reduced temperature, ϵ. Close inspection of Figure 13 reveals why the additional complexity is required in the functions for Θ and α. The shape of the α function for vapor density is not as simple as those for vapor pressure and liquid density shown in Figures 2 and 8, respectively.

Criteria of Evaluation

As already discussed, one of the desired features of the saturation property correlation is accurate representation of experimental data (within their uncertainty) over the complete saturation range. Figure 14 compares the proposed vapor density

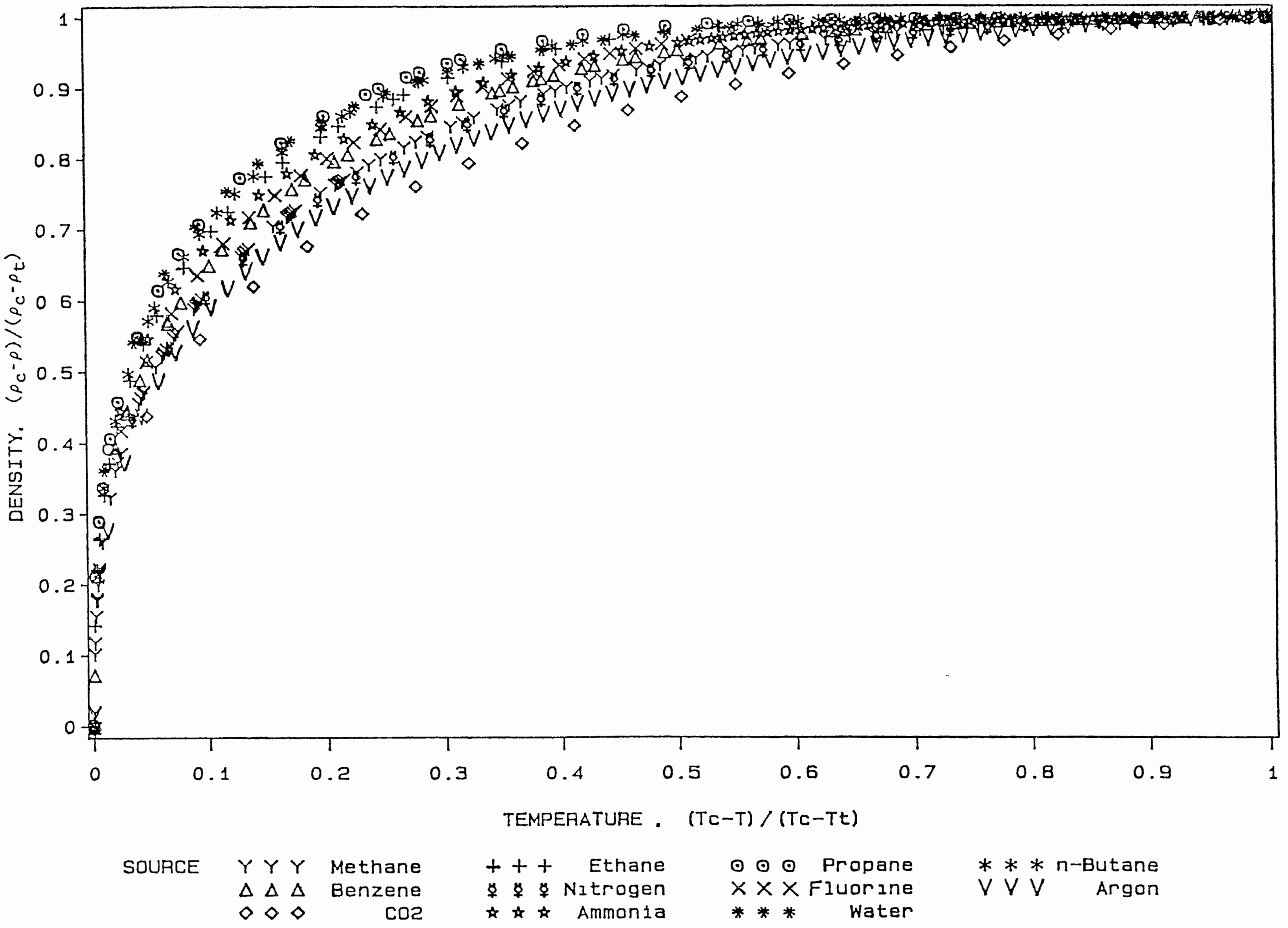

Figure 12. Saturated Vapor Density Variation with Temperature

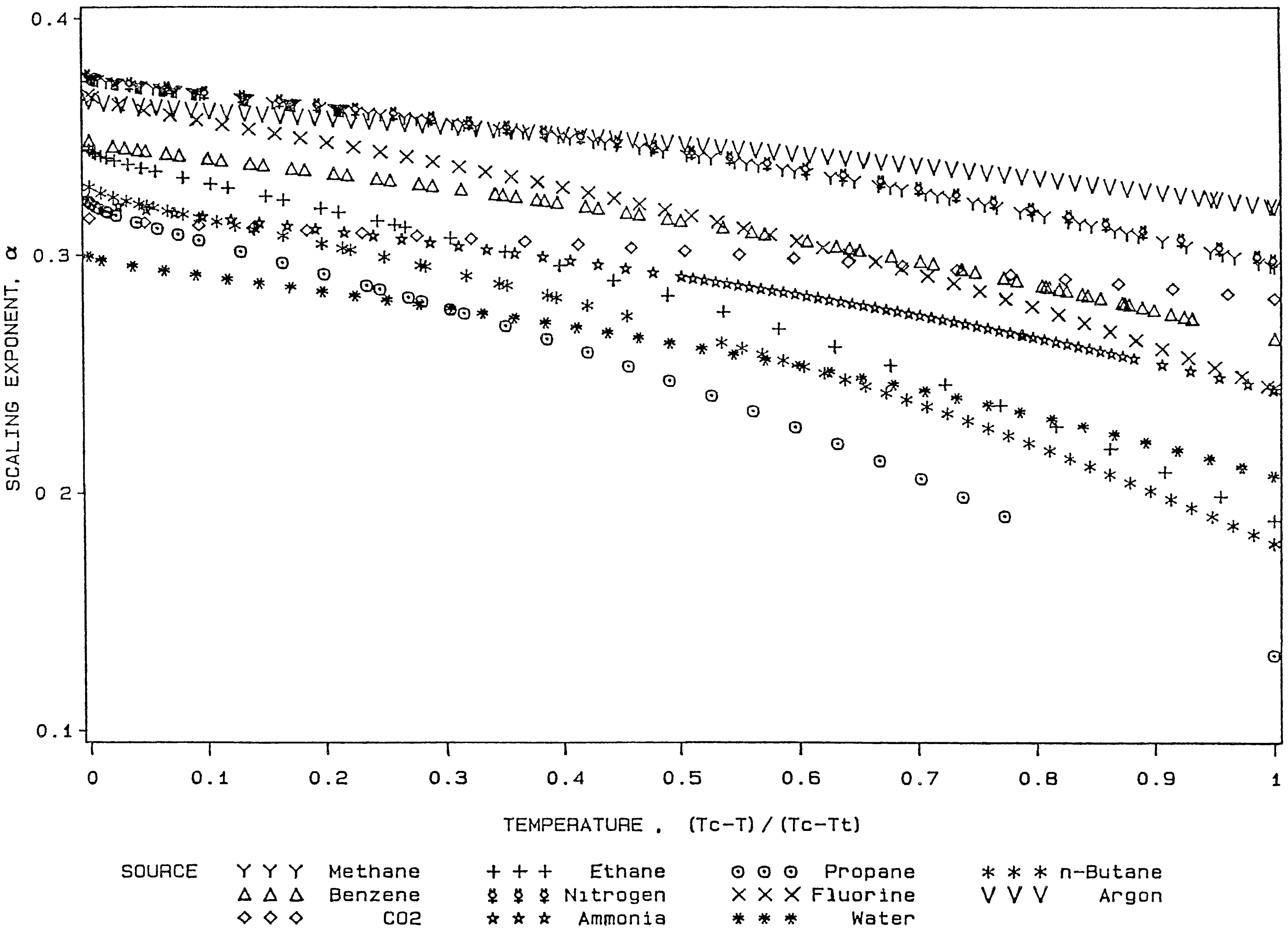

Figure 13. Effect of Temperature on the Saturated Vapor Density Scaling Exponent

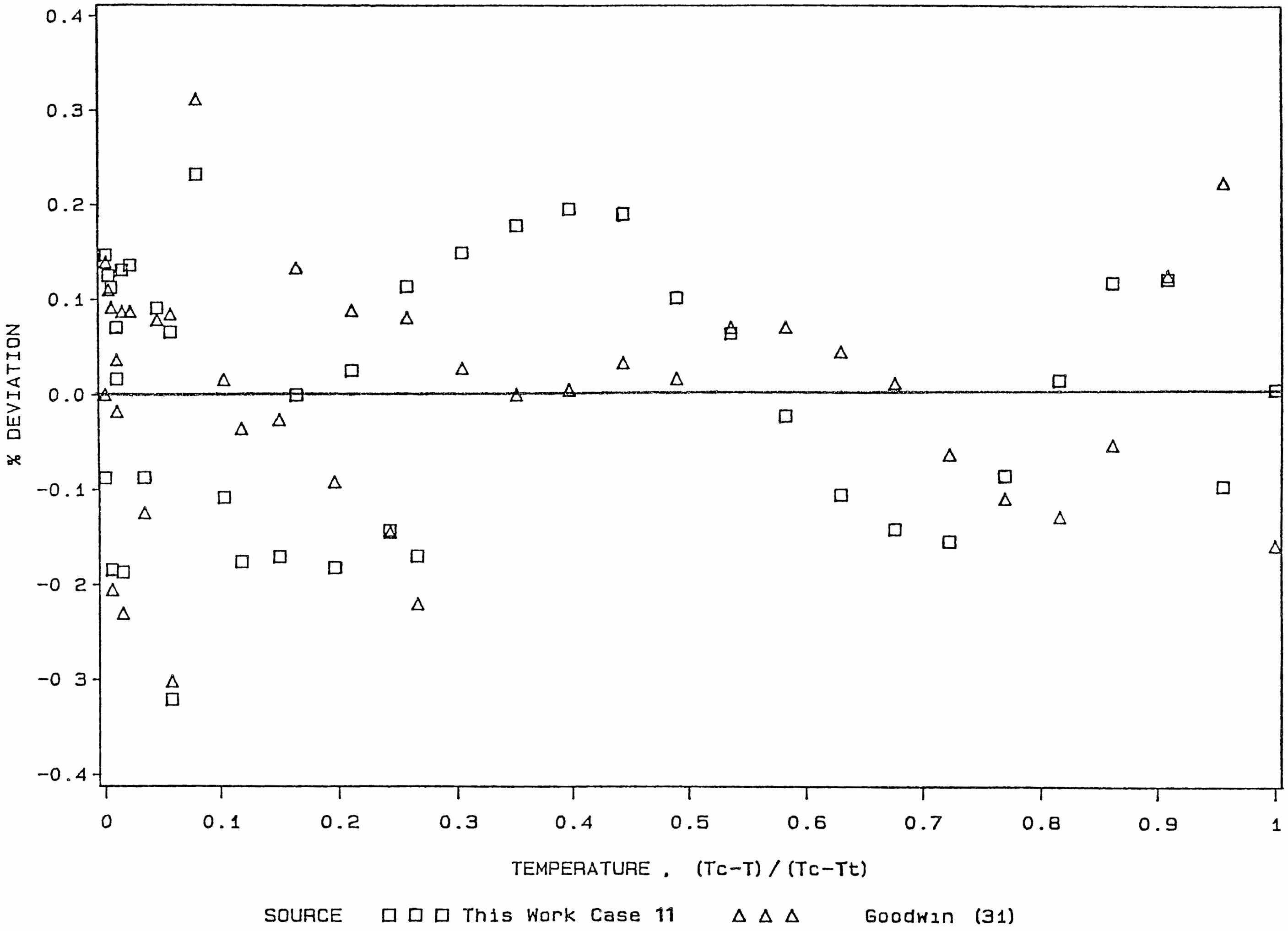

Figure 14. Comparison of Ethane Vapor Density Representations

correlation with that of Goodwin's equation (31) for ethane. The case shown is Case 11 (described in Table I) in which A_1, B_1, α_c, and $\Delta\alpha$ are treated as substance-specific parameters. Figure 14 shows that Case 11 (a four constant model) is comparable to Goodwin's six constant model.

As discussed earlier, the constraints on the behavior of density near the critical point are the same for the vapor and liquid phases. Accordingly, the vapor density model must yield a leading term with the appropriate scaling-law exponent (35). The proposed model can be expanded to provide a form similar to Equation (42) in which the leading exponent is represented by the smaller of B_1 and B_2 of Equation (46). The currently accepted value for the density critical point scaling exponent is 0.325 (35) and this is the value used for B_1 in Cases 13-15 as described in Table I.

As with the liquid density model, the proposed model, in an expanded form, produces a similar functional form to Equation (13) obtained from extended scaling theory with the added advantages of being a closed-form equation and containing parameters that appear descriptive of molecular structure.

Model Evaluation

As indicated by Equations (46) and (47), the proposed correlation contains seven parameters, A_1, A_2, B_1, B_2, C, α_c, and α_t. Present studies, however, indicate that a good level of precision may be obtained by treating some of the parameters as universal constants that apply to all fluids.

Five specific cases were studies as described in Table I and results of the first three cases (Cases 11-13) are presented in Table

VI. In Case 11, four of the model parameters (A_1, B_1, α_c, and α_t) are treated as substance-specific parameters. In Case 12, B_1, α_c, and α_t are treated as substance-specific parameters, and in Case 13, only α_c and α_t are treated as substance-specific parameters and B_1 is fixed at the theoretical scaling-law value of 0.325. Values for the regressed parameters for these cases are listed in Table C.5 of Appendix C.

Comparison of Cases 11-13 indicate that for the most accurate representation of experimental data, the flexibility offered by a four constant equation is desirable and leads to precise representation of the experimental data for the fluids considered (RMSE = 0.356 Kg/m^3 and %AAD = 0.167). By comparison, the results of Case 12 (a three constant model) show only slight deterioration in the overall quality of the fit (RMSE = 0.633 Kg/m^3 and %AAD = 0.178). Reduction of the proposed model to a two constant model as shown by Case 13 again results in only slight deterioration in the overall quality of fit (RMSE = 0.739 Kg/m^3 and %AAD = 0.200).

Extension of the proposed vapor density correlation to a preliminary generalized model through the development of generalized equations for α_c and (α_c-α_t) follows.

Preliminary Model Generalization

The development of the preliminary vapor density model generalization consisted in re-regressing the constants for each of the sets of generalized equations for α_c and $\Delta\alpha$ developed for the vapor pressure and liquid density models. The equations developed based on the vapor pressure model proved to be superior and, therefore, the equations for α_c and $\Delta\alpha$ are as follows:

TABLE VI

VAPOR DENSITY MODEL EVALUATION

Substance	This Work						Literature	
	Case 11		Case 12		Case 13		Goodwin (31)	
	RMSE, Kg/m^3	%AAD	RMSE, Kg/m^3	%AAD	RMSE, Kg/m^3	%AAD	RMSE, Kg/m^3	%AAD
Methane	0.291	0.230	0.310	0.222	0.350	0.227	0.232	0.187
Ethane	0.115	0.121	0.311	0.194	0.247	0.211	0.110	0.097
Propane	0.160	0.134	0.169	0.142	0.197	0.143	0.157	0.285
n-Butane	0.143	0.277	0.270	0.297	0.197	0.304	0.083	0.143
Benzene	0.600	0.287	0.767	0.276	0.766	0.276	0.468	0.252
Nitrogen	0.046	0.083	0.279	0.119	0.158	0.121	0.014	0.051
Fluorine	0.221	0.117	0.133	0.114	0.169	0.117	0.182	0.084
Argon	0.745	0.135	1.567	0.164	1.573	0.164	0.218	0.071
CO_2	0.014	0.009	0.203	0.088	0.680	0.111	0.003	0.004
Ammonia	0.034	0.024	0.124	0.063	0.124	0.063	0.042	0.019
Water	0.040	0.049	0.037	0.051	1.464	0.346	0.104	0.031
Overall	0.356	0.167	0.633	0.178	0.739	0.200	0.236	0.133

Case 11: A_2=0.5, B_2=1.325, C=0.7
Case 12: A_1=4.8, A_2=0.5, B_2=1.325, C=0.7
Case 13: A_1=4.8, A_2=0.5, B_1=0.325, B_2=1.325, C=0.7

$$\alpha_c = C_1 T_{rt}^{C_2} + C_3 Z_c^{C_4} + [C_3^{(Z_c-0.29)} + C_5^{\omega} + C_6^{(3\omega-\omega/Z_c)} - 3.0] \qquad (50)$$

$$(\alpha_c-\alpha_t) = C_1 T_{rt}^{C_2} + C_3 Z_c^{C_4} + (C_1-1) T_{rt}^{C_4} + [C_3^{(Z_c-0.29)} - 1.0] C_7 \qquad (51)$$

Values for the constants C_1 through C_7 are listed in Table C.6 of Appendix C. Because of the preliminary nature of this generalization, the vapor density generalization was not checked against a second database as the vapor pressure and liquid density models were. The generalization as given above works well for the fluids considered; however, the correction terms must be re-evaluated in order to accommodate strongly polar and hydrogen-bonding fluids such as alcohols and organic acids.

Results of two cases (Cases 14 and 15) based on the preliminary generalization are shown in Table VII. In Case 14, $\Delta\alpha$ is calculated from Equation (51) and α_c is treated as a single substance-specific parameter. In Case 15, α_c and $\Delta\alpha$ come from Equations (50) and (51), respectively, and the model is completely generalized.

As shown in Table VII, the generalized model results in overall %AAD of less than 1.0%. This demonstrates the viability of a generalized vapor density model which is capable of providing predictions for all classes of fluids once better equations for α_c and $\Delta\alpha$ are developed.

TABLE VII

RESULTS OF PRELIMINARY GENERALIZED VAPOR DENSITY MODEL

Substance	Case 14 RMSE, Kg/m^3	Case 14 %AAD	Case 15 RMSE, Kg/m^3	Case 15 %AAD
Methane	0.403	0.310	1.204	1.378
Ethane	0.542	0.612	0.375	0.671
Propane	0.736	1.247	0.197	1.084
n-Butane	0.394	0.552	0.608	0.896
Benzene	0.576	0.369	0.880	0.493
Nitrogen	0.112	0.122	0.118	0.310
Fluorine	1.964	0.461	1.126	1.026
Argon	1.680	0.320	2.089	1.521
Carbon Dioxide	1.824	0.673	0.822	1.450
Ammonia	0.602	0.406	0.275	0.883
Water	1.235	0.533	1.152	0.995
Overall	0.999	0.460	1.061	0.996

CHAPTER VIII

DISCUSSION

A unified treatment of the saturation properties of various chemical species is well founded in the basics of corresponding states (5,9-13). On a macroscopic basis, the two-parameter theory establishes T_c and p_c (or v_c) as reducing coordinates. This development has lead to property correlations that apply satisfactorily to simple symmetric molecules. Pitzer and co-workers (64) extended the utility of the CST approach to non-polar fluids in general by introducing a third parameter, the acentric factor, to account for size-shape effects.

The present work, as expressed by Equations (24) and (25), suggests that there are advantages in scaling the thermodynamic property prior to normalizing by the reducing coordinates such that,

$$Y_r^{\alpha} = Y(T_r, \alpha_c, \alpha_t) \tag{52}$$

Most important of these advantages is that such a variable transformation leads to simpler relationships between independent (T) and dependent (p or ρ) variables, and is a convenient means to account for variation in chemical structure.

Also, an integral element of this approach is the constraining effects of limiting the correlation range between two well-defined limits (the triple and critical points). Notice here that the choice for the lower temperature limit was dictated by the desire of having a correlation over the full saturation range.

Regarding the proposed definitions for α and Θ, the results indicate that the proposed definitions correspond with the required criteria discussed earlier. It also appears that a general function for Θ can be written as,

$$\Theta = \frac{N - \sum_{i=1}^{N} A_i \epsilon^{B_i}}{N - \sum_{i=1}^{N} A_i} \qquad (53)$$

with as many terms as necessary to accomodate the complexity of the property under consideration. In expanded forms, the proposed models contain leading exponents similar to those predicted by scaling theory. However, the proposed framework does not preclude other definitions for Θ or α if the alternative definitions prove to be better or theoretically more acceptable.

As indicated by the generalized equations for α_c and $\Delta\alpha$ for the properties considered, both Z_c and ω were employed for parameter generalization. The inadequacy of either parameter to fully characterize variation in molecular structure of anormal fluids has been documented in the past by several investigators (83-86), and attempts nave been made to overcome such shortcoming. The present study indicates that a realistic possibility exists for the development of a meaningful indexing parameter for variation in molecular structure based on α_c. Perhaps such an undertaking will facilitate generalized predictions for highly demanding molecular structures for which Z_c and ω characterization is inadequate.

The present work demonstrates the ability of the proposed model both as a correlative tool and as a framework for development of generalized predictive equations. The models for vapor pressure, saturated liquid density and saturated vapor density were all shown to be capable of representing the experimental data within their uncertainty with either three or four substance-specific parameters. While the quality of experimental data varies for the properties considered (uncertainties in vapor pressure of about 0.05 %AAD, uncertainties in liquid densities of about 0.1 %AAD and uncertainties in vapor densities of about 0.15 %AAD), generalized predictions for all three properties resulted in average errors of about 1.0 %AAD for all compounds considered.

In summary, several advantages can be cited for the proposed framework based on the evaluation of its abilities in correlating vapor pressures and saturated liquid and vapor densities, including:

1. This method offers a highly precise and efficient approach for correlating saturation properties over the full saturation range.
2. The present work demonstrates the benefits of scaling the thermodynamic variable in addition to reduction as required by the corresponding states principle.
3. The parameters of Θ and α can be defined in a manner that facilitates compliance with the theoretical requirements of scaling theory and the desired attributes of phenomenological observations.
4. The present work has demonstrated the importance of using structural parameters defined at the triple point (α_t) where

fluid behavior is highly substance-specific as well as those defined at the critical point (α_c) where fluid behavior is universal.

5. The model parameters obtained appear to have some underlying physical significance, which may be exploited in quantifying the extent of fluid polarity.
6. As demonstrated, the proposed approach is capable of providing predictive generalized correlations.

CHAPTER IX

CONCLUSIONS AND RECOMMENDATIONS

A new framework is proposed for correlating saturation properties using a scaled-variable-reduced-coordinate approach. Utility of this approach is demonstrated by the correlation of the vapor pressures and saturated liquid and vapor densities of a number of compounds at temperatures from the triple point to the critical point. New correlations based on the proposed method result in precise representation of vapor pressures (%AAD within 0.1), saturated liquid densities (%AAD within 0.1), and saturated vapor densities (%AAD within 0.2) of diverse chemical species. In addition, the proposed model compares favorably with the existing literature correlations with the added advantages of covering the full saturation range and obeying scaling-law behavior in the near-critical region.

Although the approach is essentially empirical, the results obtained suggest an underlying physical significance for the model parameters and show an excellent potential for generalized predictions. This is demonstrated by generalized equations for the model parameters in which average errors of about 1.0% are obtained for prediction of vapor pressure and saturated liquid and vapor densities.

Several issues concerning the proposed correlations remain to be resolved. The generalization for the vapor density correlation is incomplete. Because of the scarcity of good quality vapor density data available in the literature and time constraints, a second database was not compiled to test the generalized correlation. Therefore, a thorough evaluation of the proposed correlation for α_c and $\Delta\alpha$ is required.

The data for saturated liquid and vapor densities should be combined and regressed simultaneously to develop equations for the co-existing phases that are in complete agreement with the theories of scaling law in the near-critical region. Such an effort would allow construction of generalized equations for the two phase densities with the same value of α_c for both phases. Similarly, investigation should be extended to include the vapor pressure in order to produce a value for α_c that is a critical point property representative of molecular structure and polarity for each compound.

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APPENDIX A

DESCRIPTION OF LITERATURE MODELS

The following literature models are presented only to show their basic functional form and degree of complexity. This Appendix is not intended as a complete account of these correlations. The appropriate references should be referred to for more complete descriptions and details.

Vapor Pressure Correlations

Wagner (16)

$$\ln(p/p_c) = \frac{Tc}{T}(n_1\tau + n_2\tau^{1.5} + n_3\tau^3 + n_4\tau^6)$$

where $\tau = 1 - T/T_c$

n_1, n_2, n_3, n_4 = substance-specific correlation parameters.

Iglesias-Silva, et. al. (17)

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

where

$$p_0 = a_0 + a_1(a_3t + 1)^{(b/R)}\exp\left(\frac{-a_2 + b/R}{a_3t + 1}\right)$$

$$a_0 = 1 - \frac{p_t}{p_c - p_t}$$

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

$$a_2 = b_1/RT_t$$

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

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

$$a_5 = -0.11599104 + 0.29506258a_4^2 - 0.00021222a_4^5$$

$$a_6 = -0.01546028 + 0.08978160a_4^2 - 0.05322199a_4^3$$

$$a_7 = 0.05725757 - 0.06817687a_4 + 0.00047188a_4^5$$

$N = 87T_{rt}$

$\Theta = 0.2$

R = gas constant

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

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

and a_4, b, b_1 = substance-specific correlation parameters.

<u>Gomez-Nieto and Thodos (18)</u>

$$\ln(p/p_c) = \beta\left(\frac{1}{T_r^m} - 1\right) + \gamma(T_r^7 - 1)$$

where

$$s = \frac{T_b \ln(p_c)}{T_c - T_b}$$

$$m = 0.64837\exp(0.10982s) - 2725.2/[\exp(2.0133s)]$$

$$\beta = -4.39474 - \frac{9.168\text{x}10^{12}}{e^{5.95s}} + \frac{3.6529}{\exp(5473/s^{3.5})}$$

$$\gamma = -1.0668 - 0.33056s + 1.6363\exp(0.11063s)$$

Liquid Density Correlations

<u>Modified Rackett Equation (22)</u>

$$1/\rho = (RT_c/p_c)Z_{RA}^{[1+(1-T_r)^{2/7}]}$$

where

Z_{RA} is a single substance-specific parameter.

Hankinson and Thomson (21)

$$\frac{v_s}{v^*} = v_{r0}[1 - \omega v_{r1}]$$

$$v_{r0} = 1 + a(1-T_r)^{1/3} + b(1-T_r)^{2/3} + c(1-T_r) + d(1-T_r)^{4/3}$$

$$v_{r1} = [e + f(T_r) + gT_r^2 + hT_r^3]/(T_r-1.00001)$$

$a = -1.52816$

$b = 1.43907$

$c = -0.81446$

$d = 0.190454$

$e = -0.296123$

$f = 0.386914$

$g = -0.0427258$

$h = -0.0480645$

and v^* is a single substance-specific correlation parameter.

Vapor Density Correlation

Goodwin (31)

$$Y = A_1u + A_2x^{0.35} + A_3x + A_4x^{4/3} + A_5x^{5/3} + A_6x^2$$

where

$$Y = \frac{\ln(\rho_c/\rho)}{\ln(\rho_c/\rho_t)}$$

$$u = \frac{(T_c/T-1)}{(T_c/T_t-1)}$$

$$x = \frac{T_c - T}{T_c - T_t}$$

and A1, A2, A3, A4, A5, A6 = substance-specific correlation parameters.

APPENDIX B

DATABASE EMPLOYED

TABLE B.1

PHYSICAL CONSTANTS USED IN DEVELOPMENT OF THE PROPOSED VAPOR PRESSURE CORRELATION

Substance	Critical Point		Triple Point		Source
	T,K	P, bar	T,K	P, bar	
Methane	190.530	45.957	90.68	0.1174	48
Ethane	305.330	48.714	90.348	$1.131\text{x}10^{-5}$	31
Propane	369.80	42.42	85.470	$1.6808\text{x}10^{-9}$	50
Argon	150.86	48.979	83.804	0.6895	17,16
Nitrogen	126.200	34.002	63.148	0.1252	16
Benzene	562.161	48.898	278.681	$4.7823\text{x}10^{-2}$	17,51
Carbon Dioxide	304.14	73.775	216.58	5.180	40,53
Water	647.13	220.55	273.16	$6.1173\text{x}10^{-3}$	54
Fluorine	144.31	52.15	53.4811	$2.52\text{x}10^{-3}$	28
Butane	425.16	37.960	134.86	$6.736\text{x}10^{-6}$	55
Ammonia	405.4	113.04	195.48	$6.075\text{x}10^{-2}$	56
Acetone[a]	508.10	47.0	*		57
Oxygen	154.581	50.429	54.36	$1.46\text{x}10^{-3}$	56
n-Decane[a]	617.6	21.076	*		4
Hydrogen	33.18	13.13	13.95	0.072	59
Methanol[a]	512.64	80.971	*		47
Ethanol[a]	513.92	61.484	*		47
Ethylene	282.34	50.4	103.986	$1.2\text{x}10^{-3}$	66

a) The triple point vapor pressure was not available for this compound. The lowest available data point was used in place of the triple point.

TABLE B.2

SOURCES AND RANGES OF VAPOR PRESSURE DATA USED IN MODEL DEVELOPMENT

Substance	Temperature Range, K	Pressure Range, bar	Source	No. of Points
Methane	90.68 - 190.53	0.1174 - 45.957	48	43
	189.90 - 190.39	45.09 - 45.79	49	71
Ethane	90.348 - 305.33	$1.131x10^{-5}$ - 48.714	31	131
Propane	85.47 - 369.80	$1.6808x10^{-9}$ - 42.42	50	54
Argon	83.804 - 150.651	0.6895 - 48.578	16	58
Nitrogen	63.148 - 126.200	0.1252 - 34.002	16	68
Benzene	278.681 - 377.07	0.04782 - 2.000	51	28
	320.00 - 560.00	0.3205 - 47.726	52	13
Carbon	217.113 - 276.165	5.3033 - 37.7152	63	19
Dioxide	269.179 - 304.14	31.3227 - 73.775	40	37
Water	273.16 - 647.13	$6.1173X10^{-3}$ - 220.55	54	39
Fluorine	53.4811 - 144.31	$2.52x10^{-3}$ - 52.153	28	123
Butane	134.86 - 425.16	$6.736x10^{-6}$ - 37.960	55	79
Ammonia	195.48 - 405.4	0.06075 - 113.04	56	23
Acetone	259.175 - 508.10	0.04267 - 47.0	57	47
Oxygen	54.36 - 154.581	$1.46x10^{-3}$ - 50.429	56	21
n-Decane	268.148 - 490.292	$1.7x10^{-4}$ - 2.7002	58	34
Hydrogen	13.95 - 33.18	0.072 - 13.13	59	21
Methanol	288.049 - 352.776	0.09815 - 1.78306	60	7
	353.46 - 512.64	1.8300 - 80.971	47	12
Ethanol	292.772 - 362.756	0.05726 - 1.55824	60	12
	373.29 - 513.92	2.2623 - 61.484	47	14
Ethylene	104.11 - 175.84	0.00124 - 1.4551	61	31
	200.00 - 282.15	4.554 - 50.222	62	28

TABLE B.3

SOURCES OF VAPOR PRESSURE DATA USED TO TEST THE VAPOR PRESSURE GENERALIZATION

Substance	Temperature Range, K	Pressure Range, bar	Source	No. of Points
Neon	24.56 - 44.448	0.43379 - 26.64	56	23
Propylene	87.89 - 365.57	$9.5\text{x}10^{-9}$ - 46.646	56	29
o-Xylene[a]	336.610 - 418.517	0.062742 - 1.03906	68	9
	432.17 - 630.33	1.4644 - 37.318	69	20
Acetic Acid[a]	293.15 - 594.75	0.01537 - 57.84	67	30
Propanol[a]	258.15 - 536.85	0.00133 - 50.55	67	16
tert-Butanol[a]	304.15 - 356.05	0.0799 - 1.01325	70	5
	356.48 - 508.87	1.01353 - 42.32	71	13
Hydrogen Cyanide[a]	267.25 - 456.65	0.266 - 50.66	70	11
Toluene[a]	308.516 - 384.659	0.06357 - 1.03903	68	9
	398.32 - 591.79	1.5049 - 41.066	69	21
Methyl Isobutyrate[a]	284.9 - 467.5	0.034 - 11.51	72	22
Acetylene	192.4 - 308.7	1.283 - 62.47	59	14
Bromine[a]	260.0 - 584.2	0.042 - 103.4	59	17
Methyl Chloride[a]	180.0 - 416.0	0.0165 - 69.0	59	26
	416.25	66.79	73	1
Chlorine[a]	233.15 - 417.16	0.7746 - 77.11	59	20
Carbon Tetrachloride[a]	110.0 - 227.5	0.0286 - 37.45	59	13
Deuterium	18.7 - 38.34	0.1709 - 16.65	59	22
Deuterium Oxide	277.0 - 644.7	0.00668 - 218.4	59	25
n-Heptane[a]	200.0 - 540.1	$2.0\text{x}10^{-5}$ - 27.35	59	27
Refrigerant 11[a]	200.0 - 471.2	0.0043 - 44.09	59	20
Refrigerant 12[a]	170.0 - 384.95	0.00867 - 41.25	56	23
Refrigerant 13[a]	91.0 - 302.0	$3.817\text{x}10^{-6}$ - 38.70	59	23
Refrigerant 13B1[a]	170.0 - 340.2	0.059 - 39.64	59	19
Refrigerant 22[a]	150.0 - 369.3	0.0017 - 49.89	59	23
Refrigerant 23[a]	149.82 - 299.09	0.0429 - 48.36	59	16
Refrigerant 113[a]	240.0 - 487.5	0.0233 - 34.11	59	25
Refrigerant 114[a]	190.0 - 419.0	0.0058 - 32.61	59	24
Refrigerant 115[a]	199.82 - 353.09	0.1604 - 31.55	59	16
Refrigerant 500[a]	200.0 - 378.6	0.1219 - 44.26	59	19
Sulfur Dioxide[a]	200.0 - 420.0	0.02056 - 66.19	59	23
	430.8	77.83	4	1
Xenon	161.4 - 289.7	0.816 - 58.21	59	14

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a) The lowest data point for this compound is not the triple point.

TABLE B.4

PHYSICAL CONSTANTS USED IN DEVELOPMENT OF THE PROPOSED LIQUID DENSITY CORRELATION

Substance	Critical Point		Triple Point		Source
	T,K	Density Kg/m^3	T,K	Density Kg/m^3	
Methane	190.555	160.43	90.68	451.56	29
Ethane	305.33	204.48	90.348	651.92	31
Propane	369.80	218.69	85.47	732.78	50
n-Butane	425.16	227.85	134.86	735.27	55
Benzene	561.75	304.64	278.68	896.51	74
Nitrogen	126.26	314.10	63.15	869.70	66
Fluorine	144.31	573.80	53.481	1704.77	75
Argon	150.86	535.62	83.78	1414.8	76
Carbon Dioxide	304.14	467.72	216.58	1178.12	53
Ammonia	405.40	235.00	195.48	733.86	77
Methanol	512.70	274.73	175.4	904.98	59
Acetic Acid	594.75	350.60	289.80	1052.87[a]	78,4
Acetone	508.15	273.00	178.20	947.32[a]	79,4
Hydrogen Fluoride	461.15	290.00	189.58	1193.0	51
Water[b]	647.13	322.00	273.16	999.78	54
Hydrogen[b]	33.18	31.43	13.95	77.04	59
Propylene[b]	365.57	223.00	87.89	768.85	56
Neon[b]	44.448	483.00	24.56	1249.3	56
Oxygen[b]	154.581	436.10	54.36	1306.8	56
Refrigerant 12[b]	384.95	558.00	115.40	1829.29[a]	56,4
n-Decane[b]	617.55	236.00	243.5	671.10	59
Cyclohexane[b]	553.4	273.25	279.7	794.1[a]	4

a) The triple point density was not available for this compound. A value for this point was regressed from the three parameter model.

b) The last eight compounds were included in the model development, but were not included in the development of the generalized equations. These compounds served as checks on the generalized model.

TABLE B.5

SOURCES AND RANGES OF LIQUID DENSITY DATA USED IN MODEL DEVELOPMENT

Substance	Temperature Range, K	Density Range, Kg/m^3	Source	No. of Points
Methane	90.68 - 190.555	160.43 - 451.56	29	61
Ethane	90.348 - 305.33	204.48 - 651.92	31	60
Propane	85.47 - 369.80	218.69 - 732.78	50	121
n-Butane	134.86 - 425.16	227.85 - 735.27	55	73
Benzene	278.68 - 561.75	304.64 - 896.51	74	60
Nitrogen	63.15 - 126.26	314.10 - 869.70	66	33
Fluorine	53.481 - 144.31	573.80 - 1704.77	75	48
Argon	83.78 - 150.86	535.62 - 1414.8	76	70
Carbon Dioxide	216.58 - 304.14	467.72 - 1178.12	53	23
Ammonia	195.48 - 405.40	235.00 - 733.86	77	68
Methanol	175.4 - 512.7	274.73 - 904.98	59	37
Acetic Acid	293.15 - 594.75	350.60 - 1049.1	78	16
Acetone	329.25 - 508.15	273.00 - 750.00	79	10
Hydrogen Fluoride	189.58 - 461.15	290.00 - 1193.0	51	30
Water[a]	273.16 - 647.13	322.00 - 999.78	54	39
Hydrogen[a]	13.95 - 33.18	31.43 - 77.04	59	21
Propylene[a]	87.89 - 365.57	223.00 - 768.85	56	30
Neon[a]	24.56 - 44.448	483.00 - 1249.3	56	22
Oxygen[a]	54.36 - 154.581	436.10 - 1306.8	56	12
Refrigerant 12[a]	170.0 - 384.95	558.00 - 1686.1	56	14
n-Decane[a]	243.5 - 617.55	236.00 - 671.10	59	33
Cyclohexane[a]	310.93 - 510.93	509.06 - 759.44	80	7
	288.15 - 313.15	759.67 - 783.31	81	5

a) The last eight compounds were included in the model development, but were not included in development of the generalized equations. These compounds served as checks on the generalized model.

TABLE B.6

SOURCES OF LIQUID DENSITY DATA USED TO TEST THE LIQUID DENSITY GENERALIZATION

Substance	Temperature Range, K	Density Range, Kg/m^3	Source	No. of Points
Acetylene[a]	192.4 - 308.7	230.41 - 609.76	59	15
Bromine[a]	260.0 - 584.2	1179.94 - 3219.57	59	18
Methyl Chloride[a]	175.0 - 416.0	364.96 - 1131.22	59	27
Chlorine[a]	233.15 - 417.16	571.43 - 1587.30	59	20
Carbon Tetrafluoride[a]	100.0 - 227.5	625.78 - 1862.20	59	14
iso-Butane	113.6 - 408.0	224.01 - 741.29	59	24
n-Heptane	182.6 - 540.1	232.56 - 773.99	59	28
Refrigerant 13[a]	91.0 - 302.0	553.10 - 1863.24	59	23
Refrigerant 22[a]	150.0 - 369.3	496.28 - 1610.57	59	23
Sulfur Dioxide[a]	200.0 - 425.1	524.66 - 1615.77	59	24
Toluene[a]	270.0 - 591.8	291.38 - 887.31	59	25
Xenon	161.4 - 289.7	1099.99 - 2965.6	59	14

a) The lowest data point for this compound is not the triple point.

TABLE B.7

PHYSICAL CONSTANTS USED IN DEVELOPMENT OF THE PROPOSED VAPOR DENSITY CORRELATION

Substance	Critical Point		Triple Point		Source
	T,K	Density Kg/m^3	T,K	Density Kg/m^3	
Methane	190.555	160.43	90.68	0.25153	29
Ethane	305.33	204.48	90.348	$4.565\text{x}10^{-5}$	31
Propane	369.8	218.69	85.47	$1.861\text{x}10^{-8}$	50
n-Butane	425.16	227.85	134.86	$3.4916\text{x}10^{-5}$	55
Benzene	561.75	304.64	278.68	0.1617	74
Nitrogen	126.26	314.1	63.15	0.6803	66
Fluorine	144.31	573.8	53.481	0.02166	75
Argon	150.86	535.62	83.78	4.0502	76
Carbon Dioxide	304.14	467.83	216.58	13.762	53
Ammonia	405.4	235.0	195.48	0.063906	77
Water	647.13	322.0	273.16	$4.855\text{x}10^{-3}$	54

TABLE B.8

SOURCES AND RANGES OF VAPOR DENSITY DATA USED IN MODEL DEVELOPMENT

Substance	Temperature Range, K	Density Range, Kg/m^3	Source	No. of Points
Methane	90.68 - 190.555	0.25153 - 160.43	29	123
Ethane	90.348 - 305.33	4.565×10^{-5} - 204.48	31	40
Propane	85.47 - 369.8	1.861×10^{-8} - 218.69	50	42
n-Butane	134.86 - 425.16	3.4916×10^{-5} - 227.85	55	57
Benzene	278.68 - 561.75	0.1617 - 304.64	74	124
Nitrogen	63.15 - 126.26	0.6803 - 314.1	66	33
Fluorine	53.481 - 144.31	0.02166 - 573.8	75	48
Argon	83.78 - 150.86	4.0502 - 535.62	76	70
Carbon Dioxide	216.58 - 304.14	13.762 - 467.83	53	23
Ammonia	195.48 - 405.4	0.063906 - 235.0	77	68
Water	273.16 - 647.13	4.855×10^{-3} - 322.0	54	39

APPENDIX C

CORRELATION PARAMETERS

TABLE C.1

VAPOR PRESSURE CORRELATION PARAMETERS

	Case 1			Case 2		Case 3
Substance	B	α_c	$\Delta\alpha$	α_c	$\Delta\alpha$	α_c
Methane	0.985563	0.367628	0.076820	0.367095	0.077123	0.371700
Ethane	0.982571	0.286707	0.118977	0.285817	0.118164	0.285372
Propane	0.985976	0.253856	0.133578	0.254118	0.133961	0.255443
Argon	0.987831	0.403972	0.061925	0.406640	0.064018	0.414108
Nitrogen	0.987541	0.371782	0.073122	0.373573	0.074591	0.377375
Benzene	0.983012	0.337015	0.078684	0.335910	0.077850	0.337606
CO_2	0.985512	0.445291	0.042534	0.446087	0.043218	0.457551
Water	0.986568	0.274569	0.082424	0.275168	0.082894	0.276237
Fluorine	0.982217	0.323592	0.102246	0.322449	0.101325	0.322053
n-Butane	0.990349	0.270732	0.111373	0.272124	0.112467	0.271161
Ammonia	0.989999	0.312871	0.075813	0.315470	0.077826	0.315722
Acetone	0.989068	0.312321	0.067950	0.314483	0.069519	0.317348
Oxygen	0.979662	0.325301	0.107611	0.323157	0.105933	0.322093
n-Decane	0.987354	0.263208	0.087572	0.264044	0.088207	0.261443
Hydrogen	0.997330	0.389571	0.061751	0.398497	0.068486	0.414538
Methanol	0.999291	0.279051	0.057560	0.287404	0.064084	0.221509
Ethanol	1.006410	0.284439	0.069511	0.296183	0.078389	0.224465
Ethylene	0.983463	0.315356	0.104812	0.314739	0.104325	0.311464

Case 1: $A=2/3, C=4/3$
Case 2: $A=2/3, B=0.985, C=4/3$
Case 3: $A=2/3, B=0.985, C=4/3$, $\Delta\alpha$ from Equation (37)

TABLE C.2

GENERALIZED VAPOR PRESSURE CORRELATION PARAMETERS

Parameter	Value
A	2/3
B	0.985
C	4/3
C_1	0.433
C_2	1.722
C_3	0.775
C_4	0.897
C_5	0.799
C_6	0.941
C_7	2.643

TABLE C.3

LIQUID DENSITY CORRELATION PARAMETERS

	Case 6			Case 7		Case 8
Substance	A	α_c	$\Delta\alpha$	α_c	$\Delta\alpha$	α_c
Methane	1.119060	0.479863	0.112207	0.647437	0.006665	0.435407
Ethane	1.142850	0.436693	0.216771	0.568740	0.211788	0.379341
Propane	2.611240	1.099890	0.344095	0.543798	0.319112	0.356572
Butane	1.132100	0.444000	0.272154	0.582482	0.273629	0.380897
Benzene	0.996839	0.343297	0.196180	0.609486	0.189819	0.401532
Nitrogen	1.186830	0.417869	0.099689	0.531293	0.090338	0.310962
Fluorine	0.999988	0.283543	0.068485	0.547022	0.051145	0.357890
Argon	0.839481	0.058751	0.003228	0.534819	0.000051	0.315294
Carbon Dioxide	1.036500	0.350685	0.002506	0.622000	-0.027913	0.384784
Ammonia	1.007070	0.297064	0.018095	0.544497	0.003316	0.377891
Water	2.706580	1.496900	-2.207570	0.856363	-1.361430	0.816625
Hydrogen	0.827320	0.049119	-0.835918	0.589107	-1.028740	0.497705
Methanol	0.585547	0.145008	0.286887	0.822422	0.228084	0.652780
Propylene	1.174510	0.411040	0.330174	0.512190	0.335123	0.331967
Neon	0.945980	0.203411	-0.206676	0.563611	-0.268330	0.366828
Oxygen	1.181670	0.415199	0.117573	0.524581	0.112928	0.330449
Refrigerant 12	1.688020	0.752660	0.305095	0.555367	0.304232	0.364902
Acetic Acid	1.042800	0.477317	0.145933	0.684254	0.000904	0.519894
Acetone	1.146500	0.429629	0.806172	0.548103	0.836744	0.310002
n-Decane	1.145870	0.424179	-0.009054	0.554032	-0.028542	0.369567
Cyclohexane	1.152770	0.496339	0.361115	0.631257	0.363992	0.367142
Hydrogen Fluoride	1.273470	0.458965	0.521769	0.490716	0.526583	0.348649

Case 6: B=0.325
Case 7: A=4/3, B=0.325
Case 8: A=1.07068, B=0.325, $\Delta\alpha$ from Equation (44)

TABLE C.4

GENERALIZED LIQUID DENSITY CORRELATION PARAMETERS

Parameter	Value
A	1.07068
B	0.325
C_1	3.63493
C_2	-3.73713
C_3	0.32786
C_4	-0.90951
C_5	0.36141
C_6	2.95802
C_7	16.4993
C_8	-25.4640

TABLE C.5

VAPOR DENSITY CORRELATION PARAMETERS

	Case 11				Case 12			Case 13		Case 14
Substance	A_1	B_1	α_c	$\Delta\alpha$	B_1	α_c	$\Delta\alpha$	α_c	$\Delta\alpha$	α_c
Methane	4.59721	0.33755	0.36775	0.07699	0.33242	0.36252	0.07275	0.37461	0.07990	0.54645
Ethane	4.17212	0.34062	0.35917	0.16873	0.32286	0.34664	0.15761	0.34448	0.15600	0.48271
Propane	4.65540	0.32959	0.32468	0.19239	0.32625	0.32188	0.18980	0.32304	0.19087	0.44723
n-Butane	5.50615	0.31167	0.31703	0.14011	0.32730	0.32665	0.14843	0.32866	0.14984	0.45878
Benzene	5.84762	0.29704	0.33931	0.07431	0.31811	0.35800	0.08930	0.34796	0.08326	0.49332
Nitrogen	5.87072	0.30545	0.35250	0.06114	0.32553	0.37491	0.07759	0.37585	0.07813	0.54742
Fluorine	4.55948	0.32874	0.37535	0.12967	0.32274	0.37037	0.12556	0.36765	0.12378	0.52177
Argon	3.34672	0.37023	0.43686	0.09707	0.33895	0.33710	0.03081	0.36461	0.04504	0.56244
CO_2	7.21477	0.27737	0.28528	0.01110	0.30981	0.36032	0.05641	0.31549	0.03391	0.51264
Ammonia	5.61799	0.30769	0.31088	0.07033	0.32440	0.32418	0.08051	0.32340	0.08007	0.45408
Water	4.84526	0.30476	0.31992	0.10490	0.30569	0.32082	0.10564	0.29974	0.09220	0.42079

Case 11: A_2=0.5, B_2=1.325, C=0.7
Case 12: A_1=4.8, A_2=0.5, B_2=1.325, C=0.7
Case 13: A_1=4.8, A_2=0.5, B_1=0.325, B_2=1.325, C=0.7
Case 14. A_1=3.11, A_2=0.6, B_1=0.325, B_2=1.269, C=0.6, $\Delta\alpha$ from Equation (51)

TABLE C.6

GENERALIZED VAPOR DENSITY CORRELATION PARAMETERS

Parameter	Value
A_1	3.110
A_2	0.600
B_1	0.325
B_2	1.325
C	0.600
C_1	0.2998
C_2	0.4365
C_3	0.9884
C_4	0.8631
C_5	0.7532
C_6	0.9489
C_7	30.704

VITA

Ronald D. Shaver

Candidate for the Degree of

Master of Science

Thesis: A NEW SCALED-VARIABLE-REDUCED-COORDINATE FRAMEWORK FOR CORRELATION OF PURE FLUID SATURATION PROPERTIES

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Oklahoma City, Oklahoma, August 23, 1966, the son of Jim R. and Carole Shaver. Married to Kimbra Gaines on August 6, 1988.

Education: Graduated from Yukon High School, Yukon, Oklahoma, in May 1984; received Bachelor of Science Degree in Chemical Engineering from Oklahoma State University in December, 1988; completed requirements for the Master of Science Degree at Oklahoma State University in May, 1990.

Professional Experience: Employed by ARCO Oil and Gas Company as summer engineer, Summer, 1987 and 1988; Research Assistant, School of Chemical Engineering, Oklahoma State University, January, 1989 to May, 1990.
Member of American Institute of Chemical Engineers, Sigma Xi, Omega Chi Epsilon, and Tau Beta Pi.