RICE UNIVERSITY

MOLECULAR STRUCTURE EFFECTS ON THE THEORY OF CORRESPONDING STATES

by

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Abstract

A method is proposed to take into account deviations from the principle of corresponding states due to shape and size effects. Factors for use with the critical constants as reducing parameters are determined for the n-paraffin hydrocarbon series, methane through normal octane for the gas phase from second virial coefficient data. The prediction of pure component thermodynamic properties is evaluated. Applications to a vapor-liquid equilibrium calculation procedure based on composition dependent pseudo-criticals and the corresponding states theory are discussed.
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List of Symbols

a term in pseudocritical; general constant
b term in pseudocritical; general constant
B second virial coefficient
c general constant
C third virial coefficient
$C_n$ chain hydrocarbon, e.g., $C_1$ = methane
$C_p$ heat capacity
e general constant
f fugacity; function
F function
g radial distribution function; function
H enthalpy
k Boltzmann constant
K vaporization ratio, $y/x$
m exponent
n carbon number; number of components
p exponent
P pressure
r intermolecular distance
R universal gas constant
T temperature
$u$ shorthand for $(T_c/T)^{1/3}$
U internal energy
U(r) intermolecular potential energy function
V volume
x abscissa; mol fraction in the liquid; shorthand for Tc/T
Δx translational shift in x-axis
y ordinate; mol fraction in the vapor
Δy translational shift in y-axis
z compressibility factor

Greek symbols
α constant in the Θ function; exponent in pseudocritical
γ constant in the φ function
δ " " " φ "
ε force parameter (energy); constant in the φ function
θ size-shape factor for Tc
μ constant in the Θ function
π 3.14159...
ρ density
σ force parameter (length); constant in the Θ function
φ size-shape factor for Vc
ψ angle of rotation
ψ term in the K-value calculation
ω orientation variable; Pitzer's acentric factor

Superscripts
- average
\( \sim \) per mole

\( o \) reference component

' denotes corrected or pseudo-value

* ideal gas value; reduced on a molecular basis

**Subscripts**

<table>
<thead>
<tr>
<th>Subscript</th>
<th>Meaning</th>
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<tr>
<td>c</td>
<td>critical property</td>
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<td>i</td>
<td>any component</td>
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<td>j</td>
<td>any component</td>
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<td>G</td>
<td>gas phase</td>
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<td>liquid phase</td>
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<td>r</td>
<td>reference</td>
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<td>R</td>
<td>reduced by a critical constant</td>
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<td>s</td>
<td>at saturation conditions</td>
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<td>shape factor for hydrocarbon n with a reference fluid r</td>
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I. Introduction

The purpose of the present work is to take into account deviations from the corresponding states theory due to shape and size effects. As originally proposed by van der Waals, the principle is that different pure fluids obey the same equation of state in terms of reduced variables, for instance, the reduced temperature and pressure. Reduced temperature and pressure are defined by \( T_R = T/T_c \) and \( P_R = P/P_c \), where

- \( T_R \) = reduced temperature
- \( T \) = temperature
- \( T_c \) = critical temperature
- \( P_R \) = reduced pressure
- \( P \) = pressure
- \( P_c \) = critical pressure

Sufficient experimental data have since been analyzed to demonstrate that only a relatively small group of fluids obey the original corresponding states principle exactly. The molecules of these fluids are characterized by spherical shape and a two-parameter potential function dependent on separation distance only, i.e., central force interactions. For fluids which do not conform to these requirements because of structure, the interaction potential is dependent upon the relative orientations of the molecules. Deviations from corresponding states also occur in the case of polar
molecules, where electrostatic interactions cause orientational effects.

In order that corresponding states be obeyed, one must be able to write the potential functions of the various fluids in a common reduced form. Perturbation methods have been developed which treat small orientational forces as deviations from the main effect of the central forces. This approach may be applied to spherical molecules with dipole forces which are weak in comparison to the central forces. The dipolar interactions are averaged over all relative orientations of the two molecules, and the resulting potential may be superposed upon the central force potential to form the total intermolecular potential.

Orientational effects due to size and shape differences in non-polar molecules have been treated by Rowlinson using perturbation techniques. This approach is limited in applicability in that certain simplifications are necessary (such as the choice of a particular form of the intermolecular potential) in order that superposition result in a hypothetical potential which is conformal to the original central force potential.

Prigogine has developed a theorem of corresponding states for chain molecules in terms of molecular structure. A reformulation of this approach and application to the normal alkanes has been presented by Hijmans.
For certain groups of non-polar fluids with orientational effects, correlations based on an empirically defined parameter have been developed\textsuperscript{13,16}. Any group of substances with equal values of this third parameter should conform among themselves to the theory of corresponding states.

The present work determines factors for incorporation into the critical temperature and pressure in order to correct for deviations from corresponding states due to molecular size and/or shape. In essence, non-central forces are averaged over all orientations and a conformal potential is found. However, the method is based on experimental data in order to avoid the limitations which are involved in a perturbation calculation. The starting point is data for the n-paraffin hydrocarbon series, for which sufficient differences in molecular size and shape exist so as to be useful for study. Thus, a property would be expressed in terms of a universal function

\[ V_R = f \left( T_R', P_R' \right) \]

where \( T_R', P_R' \) are the corrected reduced temperature and pressure of the fluid, in contrast to the third parameter approach, \( V_R = f \left( T_R, P_R, \text{third parameter} \right) \). The advantages of using the shape factor approach over a method involving a third parameter are the following:

1. The shape factors may be used with existing combining rules for the prediction of mixture virials.
2. The shape factors may be used in a vapor-liquid equilibrium calculation procedure (Section IV-B), with an idea to extending its applicability to lower temperatures.

The disadvantages of the shape factor approach are:

1. Although shape factors are applicable over considerable ranges of density, the same factors cannot be applied at liquid densities as at moderate gas densities.

2. The shape factors are not useful in the prediction of excess functions whose derivation involves second derivatives with respect to temperature of the potential energy function, e.g., heat capacity $C_p^* - C_p$.

The size-shape factor approach is being studied for application to mixtures at low temperatures, as well as extension of the corresponding states theory to include the quantum gases.
II. Orientational Effects on the Intermolecular Potential Energy Function

In order for the corresponding states principle to apply, certain conditions must be met by the fluids in question:

1. The translational degrees of freedom of the molecules must be essentially classical.
2. The molecules are spherically symmetrical either actually, or by virtue of rapid and free rotation.
3. The internal energy of the molecules is independent of the density at any given temperature.
4. The total potential energy can be expressed as a sum of the interactions between pairs of molecules.
5. The potential energy between a pair of molecules is dependent only on their distance of separation from each other and not on their orientations.

Condition (1) will be satisfied by all fluids except those which exhibit quantum-mechanical effects in certain temperature ranges, such as hydrogen, helium, and to a lesser extent, neon. It shall be attempted to relax conditions (2) and (5) for the fluids of complex molecules by correcting for differences between these and fluids which obey the original hypothesis. However, conditions (3) and (4) must still be satisfied.

For simple fluids, if it is further postulated that the pair potential energy function is of a form containing only
two parameters such as

\[ U(r) = \varepsilon f(\frac{\sigma}{r}) \]  

(1)

where \( \varepsilon \) and \( \sigma \) have dimensions of energy and length and where \( f \) denotes a universal function, upon evaluation of the classical partition function, a universal equation of state based on this potential function is obtained. In implicit form,

\[ G(P, V, T, \sigma, \varepsilon) = 0 \]  

(2)

From dimensional analysis one can determine the dimensionless groups:

\[ P^* = \frac{P \sigma^3}{\varepsilon}, \quad V^* = \frac{V}{N \sigma^3}, \quad T^* = \frac{kT}{\varepsilon} \]  

(3)

It is then possible to write a reduced universal equation of state which is applicable to all substances conforming to the above potential function:

\[ g(P^*, V^*, T^*) = 0 \]  

(4)

If this equation must hold everywhere it must hold in particular at the critical point. The critical point is defined as that point for which both \( \frac{\partial P}{\partial V} \) and \( \frac{\partial^2 P}{\partial V^2} \) are zero; the values of the pressure, volume, and temperature at this point - the critical constants - are designated by \( P_c, V_c, T_c \). If the critical criteria are applied:

\[
\begin{bmatrix}
    g(P^*, V^*, T^*) = 0 \\
    \frac{\partial P^*}{\partial V^*} \bigg|_{T^*} = 0 \\
    \frac{\partial^2 P^*}{\partial V^*^2} \bigg|_{T^*} = 0
\end{bmatrix}
\]  

(5)

at the critical point
The solution to this set of three equations is

\[ P_c^* = P_c \frac{\sigma^3}{\varepsilon} = a \]  \hspace{1cm} (6)

\[ V_c^* = \frac{V_c}{N \sigma^3} = b \]  \hspace{1cm} (7)

\[ T_c^* = \frac{kT_c}{\varepsilon} = c \]  \hspace{1cm} (8)

where \( a, b, c \), are universal constants. It is seen that the force parameters for different fluids are proportional to the critical constants:

\[ \sigma^3 \propto V_c \]  \hspace{1cm} (9)

and

\[ \varepsilon \propto T_c \]  \hspace{1cm} (10)

Thus for fluids which meet the requirements (1) - (5) above and have a \( U(r) \) of the form postulated, the critical constants may be chosen as the characteristic parameters with which to reduce \( P, V, T \), in a universal reduced equation of state.

Let us examine the effect of relaxing conditions (2) and (5). For non-spherical molecules or non-symmetrical molecules, the potential energy of interaction may still be described as a function of distance alone, but the values of the parameters \( \varepsilon \) and \( \sigma \) will depend on the relative orientations of the two molecules. Denoting the potential function between two non-spherical molecules \( a \) and \( b \) as \( U(r_{ab}, \omega_a, \omega_b) \) where \( \omega \)
is an orientation variable, the potential energy averaged over all orientations is given by

$$\bar{U}(r_{ab}, T) = \frac{\int \int U(r_{ab}, \omega_a, \omega_b) e^{-U(r_{ab}, \omega_a, \omega_b)/kT} d\omega_a d\omega_b}{\int \int e^{-U(r_{ab}, \omega_a, \omega_b)/kT} d\omega_a d\omega_b}$$

(11)

The temperature dependence is introduced into $\bar{U}(r, T)$ through the averaging procedure. The average potential energy may be expressed in the form $\bar{U}(r, T) = \bar{c} f\left(\frac{\bar{\sigma}}{r}\right)$ where $\bar{c}$ and $\bar{\sigma}$ are temperature dependent force parameters. The use of this average potential function in the partition function will lead to proportionals of the form:

$$\bar{\sigma}^3 \propto \varphi v_c$$

$$\bar{c} \propto \Theta T_c$$

(12) (13)

where $\Theta$ and $\varphi$ are functions of temperature. As long as the same $\bar{U}(r, T)$ applies to all interactions between molecules, $\Theta$ and $\varphi$ are density independent.

Because the $U(r, \omega_a, \omega_b)$ for the fluid with non-spherical molecules can be made to conform to the $U(r)$ for the reference, then corresponding states will be obeyed. The use of the shape factors $\Theta$, $\varphi$ to correct the critical temperature and volume (the correction for critical pressure is $\frac{\Theta}{\varphi}$) should make it possible to compare the thermodynamic properties of the two pure components at the same values of reduced
temperature and volume (or pressure). For properties involving derivatives of \( \overline{U}(r,T) \) this is not rigorously true, as will be discussed in Section III-C.
III. Vapor Phase Size-Shape Factors

A. Evaluation of Factors

The classical expression for the second virial coefficient for a gas is

\[ B = 2\pi N \int_0^\infty \left( 1 - e^{-U(r)/kT} \right) r^2 dr \]  \hspace{1cm} (14)

If the two-parameter function for $U(r)$ is inserted into Equation (14) the virial coefficient can be put into reduced form

\[ \frac{B}{2\pi N\sigma^3} = f \left( \frac{kT}{\epsilon} \right) \]  \hspace{1cm} (15)

Substituting the relations (12), (13) into (15) leads to

\[ \frac{B}{\phi V_c} = f \left( \frac{T}{\Theta T_c} \right) \]  \hspace{1cm} (16)

Now, plots of reduced second virial coefficient $B/V_c$ versus reduced temperature $T/T_c$ for a group of substances which, among themselves, obey the corresponding states principle should all fall on one curve. When a reduced plot is made for a fluid of different molecular size or shape, the curve is found displaced from the first group. Moreover, in the case of paraffin hydrocarbons, the amount of displacement increases regularly with the difference in molecular shape and size. Thus, in order to obtain a universal function, any one fluid (i.e., one particular size and shape characteristic, not necessarily spherical) is chosen as reference and $\Theta$'s and $\phi$'s for other fluids can be found from the superposition
of their reduced curves upon the reference curve. This superposition insures that the form of the potential function for each fluid is the same. Then, if the virial coefficients are re-plotted as \( \frac{B}{\Theta V_c} \) versus \( \frac{T}{\Theta T_c} \), one universal curve should result.

The \( \Theta \)'s and \( \phi \)'s found in this manner will turn out to be functions of temperature only. They are the proper factors which will allow conformity to corresponding states provided that higher virials can be made up of the same interactions as exist between pairs in the second virial coefficient. At higher densities when this is not the case, the degree of error introduced is lowered because one is concerned with differences between the virial coefficients of a fluid and the corresponding virials of the reference substance, as opposed to the virials themselves.

The actual evaluation of the \( \Theta \) and \( \phi \) can be done graphically by determining the degree of translation and rotation necessary to physically superimpose one reduced virial plot upon that for the reference. In general, suppose one wishes to superimpose a plot of \( y_1 \) versus \( x_1 \) upon a plot of \( y_r \) versus \( x_r \). Then, from examination of the figure

![Graphical Representation](image-url)
it is seen that

\begin{align}
    x_r - \Delta x &= x_1 \cos \psi - y_1 \sin \psi \\
    y_r - \Delta y &= x_1 \sin \psi + y_1 \cos \psi
\end{align}

where

- \( x_1 \) = abscissa axis of the plot shifted
- \( y_1 \) = ordinate axis of the plot shifted
- \( x_r \) = abscissa axis of the reference substance
- \( y_r \) = ordinate axis of the reference substance
- \( \psi \) = angle of rotation
- \( \Delta x \) = translational shift in the \( x_r \) axis
- \( \Delta y \) = translational shift in the \( y_r \) axis

Defining \( \Theta_{i-r} = \frac{x_1}{x_r} \) and \( \phi_{i-r} = \frac{y_1}{y_r} \) one obtains

\begin{align}
    \Theta_{i-r} &= \frac{x_1}{x_1 \cos \psi - y_1 \sin \psi + \Delta x} \\
    \phi_{i-r} &= \frac{y_1}{x_1 \sin \psi + y_1 \cos \psi + \Delta y}
\end{align}

For reduced second virial coefficient plots, \( x = T_R = T/T_c \) and \( y = B/V_c \).

The accuracy of the shape factors obtained from virial curves will depend on the availability of accurate virial data. There exists a scarcity of second virial coefficient data for the heavier hydrocarbons at low temperatures.
McGlashan and Potter have compiled the available virial coefficient data on normal paraffin hydrocarbons to temperatures as low as one half the critical.

Their own data were fitted by the following equation:

$$\frac{B}{V_c} = 0.430 - 0.886 \left(\frac{T}{T_c}\right) - 0.694 \left(\frac{T}{T_c}\right)^2 - 0.0375 (n-1) \left(\frac{T}{T_c}\right)^{4.5}$$ (21)

where $n$ is the carbon number. The agreement is almost, if not quite, within experimental error. In addition, the curves calculated from Equation (21) agreed very well with the results at higher temperatures of previous investigators.

Greater precision is achieved if the shape factors are evaluated analytically from the virial coefficient equations rather than graphically. The procedure is now described.

It is desired to find the factors $\Theta$, $\phi$ which bring the normal paraffin hydrocarbons ($C_1 - C_8$) onto one function of reduced second virial coefficient versus reduced temperature:

$$\frac{B}{\phi V_c} = f \left(\frac{T}{\Theta T_c}\right)$$ (16)

The representation of $B$ as a function of $T_R$ is given by the equations of McGlashan and Potter. Now, one may choose any one of the hydrocarbon family as the reference. In the case of the McGlashan and Potter equations, however, the calculation is much simpler if methane is used as the base. Shape factors based on one reference may be converted to those on
another reference, as will be demonstrated in Section III-B.

The McGlashan and Potter equation for $C_n$ is

$$\frac{B}{V_c} = 0.430 - 0.886 \left( \frac{T_c}{T} \right) - 0.694 \left( \frac{T_c}{T} \right)^2 - 0.0375 (n-1) \left( \frac{T_c}{T} \right)^{4.5} \tag{21}$$

and for $C_1$

$$\frac{B}{V_c} = 0.430 - 0.886 \left( \frac{T_c}{T} \right) - 0.694 \left( \frac{T_c}{T} \right)^2 \tag{22}$$

Let $x = T_c/T$, $a = 0.430$, $b = -0.886$, $c = -0.694$, $e = -0.0375 (n-1)$. If the $C_1$ function is to be valid for the other hydrocarbons, then at any $T/T_c$ for $C_n$ it is required that

$$\phi_{n-1} \frac{f_{C_1}}{f_{C_n}} \left( \frac{T}{T_c} \right) = \frac{f_{C_n}}{f_{C_n}} \left( \frac{T}{T_c} \right) \tag{23}$$

That is,

$$\phi \left[ a + b \Theta x + c (\Theta x)^2 \right] = a + b x + c x^2 + e x^{4.5} \tag{24}$$

Let $u = x^{1/2}$, $x = u^2$.

For superposition of the reduced virial curves, the first, second, and higher order derivatives, for each side of Equation (24) must be the same. One accomplishes this by an expansion of the right-hand side and of the left-hand side in terms of $u$ about a certain point and equating coefficients of like-powered terms.
For the right hand side:

\[ F(u) = a + bu^2 + cu^4 + eu^6 \]
\[ F'(u) = 2bu + 4cu^3 + 9eu^8 \]
\[ F''(u) = 2bu + 12cu^2 + 9\cdot 8\cdot eu^7 \]
\[ \vdots \]
\[ F^{vi}(u) = 9\cdot 8\cdot 7\cdot 6\cdot 5\cdot 4\cdot eu^3 \]
\[ \vdots \]

etc.

The expansion is made about the point \( u = 1 \) (\( T/T_c = 1 \)):

\[ F(u) = F(u=1) + \frac{F'(u=1)}{1!}(u-1) + \frac{F''(u=1)}{2!}(u-1)^2 + \ldots \]

For left-hand side: As stated on Page 8, \( \Theta \) and \( \phi \) are functions of temperature (or \( u \)). A quadratic form is chosen:

\[ \phi = \epsilon + \alpha u + \mu u^2 \tag{25} \]
\[ \Theta = \sigma + \gamma u + \delta u^2 \tag{26} \]

where \( \epsilon, \alpha, \mu, \sigma, \gamma, \delta \) are constants to be evaluated.

Inserting these expressions into the left-hand side of Equation (24):

\[ (\epsilon + \alpha \dot{u} + \mu \ddot{u}) \left[ a + b(\sigma + \gamma \dot{u} + \delta u^2)u^2 + c(\sigma + \gamma u + \delta u^2)^2 u^4 \right] \]
Multiplying the terms out and collecting terms of like powers in \( u \), one has
\[ G(u) = A + Bu + Cu^2 + Du^3 + Eu^4 + \ldots + Ju^9 + Ku^{10} \]

where
\[
\begin{align*}
A &= a \\
B &= a \alpha \\
C &= a \mu + b \epsilon \\
D &= b \epsilon \chi + b \alpha \sigma \\
E &= b \left( \epsilon \delta + \alpha \chi + \mu \sigma \right) + c \epsilon \sigma^2 \\
&\quad \vdots \\
&\quad \vdots \\
&\quad \text{etc.}
\end{align*}
\]

\[ G'(u) = B + 2Cu + 3Du^2 + 4Eu^3 + 5Fu^4 + \ldots + 9Ju^8 + 10 Ku^9 \]

\[ G''(u) = 5 \cdot 4 \cdot 3 \cdot 2 F + 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 G + 7 \cdot 6 \cdot 5 \cdot 4 \cdot 3 Hu^2 + \ldots + 10 \cdot 9 \cdot 8 \cdot 7 \cdot 6 Ku^5 \]

\[ G(u) = G(u=1) + \frac{G'(u=1)}{1!} (u-1) + \frac{G''(u=1)}{2!} (u-1)^2 + \ldots \]

One must terminate the series after the \((u-1)^5\) term; otherwise the constants \( \epsilon, \alpha, \mu, \) etc. will be overdetermined. Of course, termination after a certain number of terms limits the range over which the \( \Theta, \Phi \) functions are applicable.
In the case at hand, the range turned out to be $0.6 < T_R < 2.0$. To increase the range of applicability, other points could have been chosen around which to make the expansion.

For convenience, $G(u)$ is rewritten as:

$$G(u) = Q + R(u-1) + S(u-1)^2 + T(u-1)^3 + ...$$

and $F(u)$ as

$$F(u) = z_1 + z_2 (u-1) + z_3 (u-1)^2 + z_4 (u-1)^3 + ...$$

Thus the six equations one must solve are:

\[
\begin{align*}
Q &= z_1 \\
R &= z_2 \\
S &= z_3 \\
T &= z_4 \\
V &= z_5 \\
W &= z_6
\end{align*}
\]

Solve by trial and error: initial values of $\xi_I, \alpha_I, \mu_I, \sigma_I, \gamma_I, \delta_I$, are chosen. Then as an approximation (linearizing), where subscript $I$ denotes first trial,

\[
\begin{align*}
Q_I + \frac{\partial Q}{\partial \xi} \xi_I + \frac{\partial Q}{\partial \alpha} \alpha_I + \frac{\partial Q}{\partial \mu} \mu_I + ... &= z_1 \\
R_I + \frac{\partial R}{\partial \xi} \xi_I + \frac{\partial R}{\partial \alpha} \alpha_I + \frac{\partial R}{\partial \mu} \mu_I + ... &= z_2
\end{align*}
\]
Six linear equations are to be solved with the unknowns being the differences

\[ \varepsilon - \varepsilon_I, \ \alpha - \alpha_I, \ \mu - \mu_I, \ \sigma - \sigma_I, \ \gamma - \gamma_I, \ \delta - \delta_I \]

The matrix elements are

\[
\begin{pmatrix}
Q_\varepsilon & Q_\alpha & Q_\mu & Q_\sigma & Q_\gamma & Q_\delta & z_1 - Q_I \\
R_\varepsilon & R_\alpha & R_\mu & R_\sigma & R_\gamma & R_\delta & z_2 - R_I \\
S_\varepsilon & S_\alpha & S_\mu & S_\sigma & S_\gamma & S_\delta & z_3 - S_I \\
T_\varepsilon & T_\alpha & T_\mu & T_\sigma & T_\gamma & T_\delta & z_4 - T_I \\
V_\varepsilon & V_\alpha & V_\mu & V_\sigma & V_\gamma & V_\delta & z_5 - V_I \\
W_\varepsilon & W_\alpha & W_\mu & W_\sigma & W_\gamma & W_\delta & z_6 - W_I
\end{pmatrix}
\]

where

\[ Q_\varepsilon = \left( \frac{\partial Q}{\partial \varepsilon} \right)_I, \quad R_\alpha = \left( \frac{\partial R}{\partial \alpha} \right)_I, \quad \text{etc.} \]

The procedure is to solve the matrix, and use the solution to get second trials, i.e.,

\[ \varepsilon_{II} = \varepsilon_I + (\varepsilon - \varepsilon_I) \]
\[ \alpha_{II} = \alpha_I + (\alpha - \alpha_I) \]

The calculation is repeated with the new trial values until the differences are less than a previously specified amount.

The matrix was solved on the Rice Computer with \( n \), the carbon number, as a parameter. Once the constants in (25) and (26) were determined, it was a simple matter to calculate the \( \Theta \)'s and the \( \phi \)'s as a function of \( T_R \).
B. Shape Factor Algebra

The above shape factors are based on \( n = 1 \) as a reference. The relations necessary in order to convert \( \Theta \)'s to any other base can be demonstrated from the sketch below. The corresponding relations for \( \phi \)'s are the same, and may be shown in a similar fashion.

The calculations above give, for example, \( \Theta_{5-1} \) at any \( x_5 \), \( \Theta_{8-1} \) at any \( x_8 \) and so on. Now, given any particular point \( x_1 \), by definition,

\[
x_1 = \frac{x_5}{\Theta_{5-1}}; \quad \text{also,} \quad x_1 = \frac{x_8}{\Theta_{8-1}}
\]

\[
\frac{x_5}{\Theta_{5-1}} = \frac{x_8}{\Theta_{8-1}}
\]

\[
\frac{x_5}{x_8} = \frac{\Theta_{5-1}}{\Theta_{8-1}}
\]
But \( \frac{x_5}{x_8} = \Theta_{5-8} \). Thus \( \Theta_{5-8} = \frac{\Theta_{5-1}}{\Theta_{8-1}} \) where \( \Theta_{5-8} \) is the shape factor for \( C_5 \) with reference \( C_8 \) at the \( T_R \) of \( C_5 \).

Since \( \frac{x_8}{x_5} = \Theta_{8-5} \),

\[
\Theta_{8-5} = \frac{\Theta_{8-1}}{\Theta_{5-1}} ,
\]

that is,

\[
\Theta_{8-5} = \frac{1}{\Theta_{5-8}}
\]

where \( \Theta_{8-5} \) is the shape factor for \( C_8 \) on a \( C_5 \) reference at the \( T_R \) for \( C_8 \).

The results for the \( \Theta \)'s are shown on Figure I, for the \( \phi \)'s on Figure II, as well as in tabular form in Table I. In order to facilitate the use of the \( \Theta \)'s and \( \phi \)'s for fluids other than those presently being considered, the shape factors are correlated with Pitzer's \( \omega \) acentric factor as shown on Figure III and Figure IV.

C. Prediction of Thermodynamic Properties for the Gas Phase

The critical constants modified with the size-shape factors developed above should be the parameters with which the universal reduced equation of state concept may be extended to complex molecules. However, the fact that the \( \Theta \) and \( \phi \) are temperature dependent introduces a further consideration. The thermodynamic properties of interest for two non-similar fluids should compare at the same values of reduced temperature and pressure, provided that these properties involve
FIG. I - VAPOR SHAPE FACTOR FOR $T_c$ (based on n-Pentane)
FIG. II - VAPOR SHAPE FACTOR FOR $V_c$ (based on n-Pentane)
### Table I. \( \Theta, \phi \) for the Vapor Phase Based on N-Pentane

For \( C_5 \), \( \Theta = 1.0 \) and \( \phi = 1.0 \)

<table>
<thead>
<tr>
<th>( T_R )</th>
<th>( C_1 )</th>
<th>( C_2 )</th>
<th>( C_3 )</th>
<th>( C_4 )</th>
<th>( C_5 )</th>
<th>( C_6 )</th>
<th>( C_7 )</th>
<th>( C_8 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>.798</td>
<td>1.285</td>
<td>.888</td>
<td>1.084</td>
<td>.941</td>
<td>1.035</td>
<td>.975</td>
<td>0.997</td>
</tr>
<tr>
<td>0.8</td>
<td>.822</td>
<td>1.272</td>
<td>.902</td>
<td>1.093</td>
<td>.948</td>
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<td>.978</td>
<td>1.004</td>
</tr>
<tr>
<td>0.9</td>
<td>.842</td>
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<td>.913</td>
<td>1.097</td>
<td>.954</td>
<td>1.035</td>
<td>.981</td>
<td>1.009</td>
</tr>
<tr>
<td>1.0</td>
<td>.860</td>
<td>1.251</td>
<td>.922</td>
<td>1.099</td>
<td>.959</td>
<td>1.038</td>
<td>.983</td>
<td>1.011</td>
</tr>
<tr>
<td>1.1</td>
<td>.875</td>
<td>1.240</td>
<td>.931</td>
<td>1.098</td>
<td>.963</td>
<td>1.040</td>
<td>.985</td>
<td>1.012</td>
</tr>
<tr>
<td>1.2</td>
<td>.888</td>
<td>1.230</td>
<td>.938</td>
<td>1.097</td>
<td>.967</td>
<td>1.041</td>
<td>.987</td>
<td>1.013</td>
</tr>
<tr>
<td>1.3</td>
<td>.899</td>
<td>1.221</td>
<td>.944</td>
<td>1.096</td>
<td>.970</td>
<td>1.041</td>
<td>.988</td>
<td>1.014</td>
</tr>
<tr>
<td>1.4</td>
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<td>.950</td>
<td>1.095</td>
<td>.973</td>
<td>1.041</td>
<td>.989</td>
<td>1.015</td>
</tr>
<tr>
<td>1.5</td>
<td>.920</td>
<td>1.204</td>
<td>.956</td>
<td>1.093</td>
<td>.976</td>
<td>1.041</td>
<td>.990</td>
<td>1.015</td>
</tr>
<tr>
<td>1.6</td>
<td>.928</td>
<td>1.196</td>
<td>.961</td>
<td>1.091</td>
<td>.979</td>
<td>1.041</td>
<td>.990</td>
<td>1.016</td>
</tr>
<tr>
<td>1.7</td>
<td>.937</td>
<td>1.189</td>
<td>.965</td>
<td>1.089</td>
<td>.982</td>
<td>1.040</td>
<td>.991</td>
<td>1.016</td>
</tr>
<tr>
<td>1.8</td>
<td>.944</td>
<td>1.182</td>
<td>.969</td>
<td>1.087</td>
<td>.983</td>
<td>1.040</td>
<td>.992</td>
<td>1.014</td>
</tr>
</tbody>
</table>
FIG. III - VAPOR SHAPE FACTOR FOR $T_c$ (based on n-Pentane) CORRELATED WITH $\omega$
FIG. IV – VAPOR SHAPE FACTOR FOR $V_c$ (based on n-Pentane) CORRELATED WITH $\omega$
no temperature derivatives of the partition function. Examples of such properties are the Helmholtz free energy and the compressibility factor. The fugacity/pressure ratio is another example; even though its evaluation requires derivatives of the partition function, none are with respect to temperature. Thermodynamic functions such as enthalpy, entropy, or internal energy, on the other hand, do involve temperature derivatives of the partition function, and hence of the intermolecular potential energy. This means that additional terms involving \(\frac{d\Theta}{dT}\) and \(\frac{d\Phi}{dT}\) arise in the expressions for these thermodynamic properties. For the reference fluid these terms vanish, and the values of the thermodynamic properties such as enthalpy, obtained from charts for the reference fluid will be in error by the amount of these terms.

**D. Prediction of \(z\) and \(f/P\)**

Table II presents the results of an attempt to predict compressibility factors and fugacity/pressure ratios for \(C_1\), \(C_3\), and \(C_7\) using thermodynamic property charts and tables based on \(C_5\). The experimental \(f/P\) and \(z\) at a given \((T_R)_n\) and \((P_R)_n\) can be compared either with the value read at \((T_R)_n/\Theta\) \(_{n-5}\), \((P_R)_n/(\Theta/\Phi)\) \(_{n-5}\) from the tables of Hougen, Watson and Ragatz \(^5\) for \(z_c = .27\), or from pentane data at \(T_5\) and \(P_5\) where \(T_5 = \left[(T_R)_n/(\Theta)\right]_{n-5}(T_0)\) \(_5\) and \(P_5 = \left[(P_R)_n/(\Phi)\right]_{n-5}(P_c)\) \(_5\).

The Hougen-Watson-Ragatz tables do not by any means correspond


<table>
<thead>
<tr>
<th>TABLE II. PREDICTION OF $f/P$ AND $z$ USING VAPOR-PHASE SHAPE FACTORS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>METHANE:</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$T = -100^\circ F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>25</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>100</td>
</tr>
<tr>
<td>200</td>
</tr>
<tr>
<td>400</td>
</tr>
<tr>
<td>600</td>
</tr>
<tr>
<td>800</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$T = -220^\circ F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>30</td>
</tr>
<tr>
<td>40</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>60</td>
</tr>
</tbody>
</table>
TABLE II. (Cont'd.)

PROPAINE:

\[ T = 240°F \]

<table>
<thead>
<tr>
<th>P</th>
<th>Experimental</th>
<th>Predicted using ( \text{C}_5 ) data</th>
<th>Predicted using ( \text{C}_5 ) data</th>
</tr>
</thead>
<tbody>
<tr>
<td>psia</td>
<td>( z )</td>
<td>( z )</td>
<td>( f/P )</td>
</tr>
<tr>
<td>100</td>
<td>.951</td>
<td>.952</td>
<td>.959</td>
</tr>
<tr>
<td>200</td>
<td>.918</td>
<td>.964</td>
<td>.906</td>
</tr>
<tr>
<td>300</td>
<td>.843</td>
<td>.808</td>
<td>.861</td>
</tr>
<tr>
<td>400</td>
<td>.778</td>
<td>.75</td>
<td>.815</td>
</tr>
<tr>
<td>500</td>
<td>.708</td>
<td>.75</td>
<td>.77</td>
</tr>
<tr>
<td>600</td>
<td>.625</td>
<td>.685</td>
<td>.725</td>
</tr>
<tr>
<td>700</td>
<td>.5</td>
<td>.5</td>
<td>.675</td>
</tr>
<tr>
<td>800</td>
<td>.48</td>
<td>.48</td>
<td>.63</td>
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</tbody>
</table>

\[ T = 100°F \]

<table>
<thead>
<tr>
<th>P</th>
<th>( z (18) )</th>
<th>( z (18) )</th>
<th>( f/P (3) )</th>
<th>( f/P (18) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>psia</td>
<td>( z ) (18)</td>
<td>( z ) (18)</td>
<td>( f/P (3) )</td>
<td>( f/P (18) )</td>
</tr>
<tr>
<td>50</td>
<td>.952</td>
<td>.952</td>
<td>.955</td>
<td>.955</td>
</tr>
<tr>
<td>100</td>
<td>.918</td>
<td>.902</td>
<td>.908</td>
<td>.910</td>
</tr>
<tr>
<td>150</td>
<td>.843</td>
<td>.84</td>
<td>.86</td>
<td>.865</td>
</tr>
<tr>
<td>188.7</td>
<td>.772</td>
<td>.788</td>
<td>.828</td>
<td>.831</td>
</tr>
</tbody>
</table>

\[ T = 40°F \]

<table>
<thead>
<tr>
<th>P</th>
<th>( z (11) )</th>
<th>( z (18) )</th>
<th>( f/P (3) )</th>
<th>( f/P (18) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>psia</td>
<td>( z ) (11)</td>
<td>( z ) (18)</td>
<td>( f/P (3) )</td>
<td>( f/P (18) )</td>
</tr>
<tr>
<td>20</td>
<td>.979</td>
<td>.975</td>
<td>.975</td>
<td>.975</td>
</tr>
<tr>
<td>40</td>
<td>.936</td>
<td>.945</td>
<td>.950</td>
<td>.948</td>
</tr>
<tr>
<td>60</td>
<td>.89</td>
<td>.915</td>
<td>.924</td>
<td>.923</td>
</tr>
<tr>
<td>79</td>
<td>.875</td>
<td>.886</td>
<td>.899</td>
<td>.899</td>
</tr>
</tbody>
</table>
TABLE II. (Cont'd.)

N-HEPTANE:

Note: z's are calculated from volumes given in Stuart, Yu, and Coull\(^{19}\)
f/P's are calculated from \(\omega\) charts in Edmister\(^2\); p. 201, 202, 203

\[
T = 600^\circ F
\]

<table>
<thead>
<tr>
<th>P atm.</th>
<th>(z)</th>
<th>(z)</th>
<th>(f/P)</th>
<th>(f/P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.956</td>
<td>.99</td>
<td>.989</td>
<td>.99</td>
</tr>
<tr>
<td>5</td>
<td>.945</td>
<td>.952</td>
<td>.955</td>
<td>.954</td>
</tr>
<tr>
<td>10</td>
<td>.907</td>
<td>.899</td>
<td>.908</td>
<td>.908</td>
</tr>
<tr>
<td>15</td>
<td>.845</td>
<td>.844</td>
<td>.865</td>
<td>.862</td>
</tr>
<tr>
<td>20</td>
<td>.791</td>
<td>.78</td>
<td>.82</td>
<td>.816</td>
</tr>
<tr>
<td>25</td>
<td>.73</td>
<td>.705</td>
<td>.776</td>
<td>.77</td>
</tr>
<tr>
<td>30</td>
<td>.646</td>
<td>.622</td>
<td>.736</td>
<td>.745</td>
</tr>
<tr>
<td>40</td>
<td>.485</td>
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<td>.633</td>
</tr>
<tr>
<td>50</td>
<td>.432</td>
<td>.37</td>
<td>.567</td>
<td>.55</td>
</tr>
<tr>
<td>60</td>
<td>.419</td>
<td>.36</td>
<td>.501</td>
<td>.49</td>
</tr>
<tr>
<td>100</td>
<td>.516</td>
<td>.512</td>
<td>.385</td>
<td>.37</td>
</tr>
</tbody>
</table>

\[
T = 450^\circ F
\]

<table>
<thead>
<tr>
<th>P atm.</th>
<th>(z)</th>
<th>(z) ((18))</th>
<th>(f/P)</th>
<th>(f/P) ((18))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.996</td>
<td>.982</td>
<td>.984</td>
<td>.982</td>
</tr>
<tr>
<td>5</td>
<td>.94</td>
<td>.911</td>
<td>.919</td>
<td>.916</td>
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<tr>
<td>10</td>
<td>.814</td>
<td>.808</td>
<td>.834</td>
<td>.839</td>
</tr>
<tr>
<td>15</td>
<td>.707</td>
<td>.668</td>
<td>.744</td>
<td>.756</td>
</tr>
</tbody>
</table>
exactly to \( C_5 \) \((z_c = .269)\) over the entire \( T_R, P_R \) range for every one of the tabulated thermodynamic functions, so that \( C_5 \) data was used for the comparison where possible. It will be noted that the agreement in all cases is good for low pressures, but becomes poorer as pressure (i.e., density) increases. At the higher densities, the increasing deviation is an indication that higher order virials can no longer be made up of the same pair interactions as the second virial coefficient. Since the method depends on the difference between corresponding virials, the more similar in structure a fluid is to the reference, the higher in density one may go before the size-shape factors fail. This may be seen from the results of Table II. For \( C_1 \) \((-100^\circ F, 600 \text{ psia})\), an 11\% deviation for \( z \) occurs at conditions corresponding to a \( C_5 \) reduced density of 0.395. For \( C_3 \) \((240^\circ F, 600 \text{ psia})\), a 9.6\% deviation occurs at conditions corresponding to a \( C_5 \) reduced density of .393. For \( C_7 \) \((600^\circ F, 40 \text{ atm})\), a 7.2\% deviation occurs at conditions corresponding to a \( C_5 \) reduced density of 0.882.

E. Prediction of Enthalpy Excess

As stated above, one cannot expect to obtain correct prediction of the enthalpy excess \( H^*-H \) by the same procedure as used for \( f/P \) and \( z \). For the sake of interest, however, a number of values were calculated using a pentane reference.
The per cent deviations, \( \frac{\text{Calc.}(H^*-H) - \text{Exp.}(H^*-H)}{\text{Exp.}(H^*-H)} \times 100 \) are summarized:

<table>
<thead>
<tr>
<th>Temperature (°F)</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>-7</td>
</tr>
<tr>
<td>600</td>
<td>+8</td>
</tr>
<tr>
<td>900</td>
<td>+5.3</td>
</tr>
<tr>
<td>1500</td>
<td>-8.2</td>
</tr>
</tbody>
</table>

The magnitudes of the deviations for methane at -100°F and -150°F were somewhat greater. The deviations for propane were in general less than for methane, but the non-regularity of the deviations persisted.

The enthalpy excess over the ideal gas value, when written in terms of the virial coefficients, involves both \( B \) and \( \frac{dB}{dT} \), \( C \) and \( \frac{dC}{dT} \), etc. On the other hand, \( U^* - U \) involves only \( \frac{dB}{dT} \), \( \frac{dC}{dT} \) and so on. It is proposed to take advantage of this fact by developing factors \( \Theta' \), \( \phi' \) for the prediction of thermodynamic properties involving only the first temperature derivative of the virial coefficients, such as \( U^* - U \). Then the enthalpy may be found from

\[
H^* - H = U^* - U + RT(1-z) \tag{29}
\]

For the compressibility factor \( z \), the original shape factors \( \Theta \) and \( \phi \) are applicable. The validity of the \( \Theta' \) and \( \phi' \) values depends on certain assumptions, as will now be demonstrated.

The expression for the temperature derivative of the
second virial coefficient is the following:

\[
\frac{dB}{dT} = 2\pi N \int_{0}^{\infty} e^{-\frac{U(r,T)}{kT}} \frac{d}{dT} \left( \frac{U(r,T)}{kT} \right) r^2 dr
\]  

It is assumed that the potential energy function is of the form

\[
U(r,T) = \xi f \left( \frac{\sigma}{r} \right)
\]  

and also that

\[
f \left( \frac{\sigma}{r} \right) = \left( \frac{\sigma}{r} \right)^m - \left( \frac{\sigma}{r} \right)^p
\]

where \( m > p \).

In terms of the critical constants and \( \Theta \) and \( \phi \),

\[
\xi = a \Theta T_c \quad \text{and} \quad \sigma^3 = b \phi v_c.
\]

Thus,

\[
U(r,T) = a \Theta T_c \left[ \left( \frac{b \phi v_c}{r} \right)^{1/3} \right]^m - \left( \frac{b \phi v_c}{r} \right)^{1/3} \left[ \left( \frac{b \phi v_c}{r} \right)^{1/3} \right]^p
\]

If \( f \left( \frac{\sigma}{r} \right) \) has the form indicated in (32), then

\[
\frac{df}{dT} \left( \frac{\sigma}{r} \right) = \left[ m \left( \frac{b \phi v_c}{r} \right)^{1/3} \right]^m - p \left( \frac{b \phi v_c}{r} \right)^{1/3} \left[ \left( \frac{b \phi v_c}{r} \right)^{1/3} \right]^p \left( \frac{d\phi}{dT} \right)
\]
or

\[
\frac{d f(\frac{\sigma}{r})}{dT} = \frac{p}{3} f(\frac{\sigma}{r}) \frac{1}{\phi} \frac{d\phi}{dT} + \left(\frac{m-p}{3}\right) \left(\frac{b\phi V_c}{r}\right)^{1/3} \frac{1}{\phi} \frac{d\phi}{dT} \tag{35}
\]

Substitution into (30), multiplication of both sides by T, and rearrangement into dimensionless form gives:

\[
\frac{T \frac{dB}{dT}}{V_c \left[\frac{\phi T^2}{\Theta} \frac{d\Theta/T}{dT} + \frac{p}{3} T \frac{d\phi}{dT}\right]} = 2\pi Nb \int_{0}^{\infty} e^{-\frac{\Theta T C}{kT} f(\frac{\sigma}{r})} \frac{\Theta T C}{kT} f(\frac{\sigma}{r}) \left(\frac{r}{\sigma}\right)^2 \frac{d(r)}{\sigma}\tag{36}
\]

\[
+ \frac{\left(\frac{m-p}{3}\right) \frac{d\phi}{dT}}{\left[\frac{\phi T^2}{\Theta} \frac{d\Theta/T}{dT} + \frac{p}{3} T \frac{d\phi}{dT}\right]} \left[2\pi Nb \int_{0}^{\infty} e^{-\frac{\Theta T C}{kT} f(\frac{\sigma}{r})} \frac{\Theta T C}{kT} (\frac{r}{\sigma})^m (\frac{r}{\sigma})^2 \frac{d(r)}{\sigma}\right]
\]

If the repulsive part of \( f \), that is, \( \left(\frac{\sigma}{r}\right)^m \) can be assumed to have a step function form:

\[
\left(\frac{\sigma}{r}\right)^m = \infty \quad \frac{r}{\sigma} < 1
\]

and

\[
\left(\frac{\sigma}{r}\right)^m = 0 \quad \frac{r}{\sigma} \geq 1
\]

then in (36) the second integral vanishes. One then has for \( \phi' \) the expression

\[
\phi' = \left[ \frac{\phi T^2}{\Theta} \frac{d\Theta}{dT} + \frac{p}{3} \cdot T \frac{d\phi}{dT} \right]
\]

while \( \Theta' = \Theta \). Since \( p \) is unknown, the value of \( \phi' \) must be found from known \( \frac{dB}{dT} \) values, using the McGlashan equations. These values are only approximations because of the assumptions.
involved. A superposition technique is presently being carried out in this laboratory, which will require an iterative calculation. The approximate values are useful as first trials in the iteration.
IV. Outline of Future Work

Further studies should be undertaken in order to continue development of the size-shape factor approach. These include:

1. Determination of relative size-shape factors for the liquid phase.

2. Extending the applicability of an existing calculation procedure for the prediction of vapor-liquid equilibrium to mixtures of dissimilar molecules through the use of size-shape factors.

A. Liquid Phase Size-Shape Factors

Many applications require the development of size-shape factors for the liquid phase. The total potential energy is assumed to be the sum of pair interactions only. With increasing density however, the $U(r)$ for a pair of molecules is no longer independent of its neighbors, and the factors found from second virial coefficients are not applicable. At high densities the potential energy functions must be changed if the pair-wise additivity is to be retained. This leads to a separate set of shape factors for liquid phase correspondence.

The expression for the compressibility factor $z$ in terms of the radial distribution function $g(T, \rho, r)$ is

$$z = 1 - \frac{2\pi}{kT} \rho \int_0^\infty r \frac{dU(r)}{dr} g(T, \rho, r) r^2 dr$$
At saturation,

\[ z_s = 1 - \frac{2\pi}{kT} \int_0^\infty r \frac{dU(r)}{dr} g(T_s, \rho_s, r) r^2 dr \]

With the assumption that the integrals containing the radial distribution function are independent of density

\[ \int_0^\infty r \frac{dU(r)}{dr} g(T, \rho, r) r^2 dr = F(T_R) \]

Thus, at constant temperature

\[ z - z_s = \frac{-2\pi}{kT} (\rho - \rho_s) F(T_R) \]

Similarly

\[ \frac{P_R - P_{R_s}}{P_R - P_{R_s}} = (\rho - \rho_s) \left[ \frac{kT}{P_c} - \frac{2\pi}{3P_c} F(T_R) \right] \]

The ratio \( \frac{z - z_s}{P_R - P_{R_s}} \) is seen to be a function of \( T_R \) only

\[ \frac{z - z_s}{P_R - P_{R_s}} = \frac{-2\pi}{kT} \frac{F(T_R)}{\frac{kT}{P_c} - \frac{2\pi}{3P_c} F(T_R)} = f(T_R) \]
Table III shows the values of this ratio for various $T_R$'s for n-pentane.

**TABLE III. VALUES OF $z - z_s$ FOR N-PENTANE**

<table>
<thead>
<tr>
<th>$T_R$</th>
<th>$P_R - P_{Rs}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.96</td>
<td>0.142</td>
</tr>
<tr>
<td>0.90</td>
<td>0.142</td>
</tr>
<tr>
<td>0.80</td>
<td>0.142</td>
</tr>
<tr>
<td>0.60</td>
<td>0.163</td>
</tr>
<tr>
<td>0.50</td>
<td>0.182</td>
</tr>
</tbody>
</table>

The numbers were calculated using the $z_c = 0.27$ tables of Hougen-Watson-Ragatz. At any given $T_R$, the value of the ratio varied only slightly with $P_R$. Some deviation was noted for $P_R$'s near the saturation $P_{Rs}$, but this was attributed to inaccuracies inherent in working with small differences. Superposition of plots of $\frac{z - z_s}{P_R - P_{Rs}}$ versus $T_R$ should yield a common curve

$$\frac{z - z_s}{(\frac{\partial}{\partial \tau}) \cdot (P_R - P_{Rs})} = f\left(\frac{T_R}{\theta_L}\right)$$

and hence liquid shape factors. Examination of this method in continuing in this laboratory.
B. Prediction of Vapor-Liquid Equilibria

The reduced properties of mixtures as a function of the true critical properties of the mixture do not give the same functional relations as found for the pure components. In order that the properties of a mixture might be found from functions derived from the pure components, several values for the pseudo-critical constants of mixtures have been proposed in terms of the critical properties of the separate components.

A method has been developed for the prediction of vapor-liquid equilibrium in mixtures from composition-dependent pseudo-criticals and the corresponding states principle. An earlier derivation of the pseudo-criticals was based on gaseous mixtures. The same pseudo-critical expressions were demonstrated theoretically to be applicable to liquids as well as gases, if in addition to the corresponding states requirements, it was assumed that the integrals containing the radial distribution function are relatively independent of density and composition. The expressions obtained are

\[
T_c' = \left( \frac{\sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j a_i a_j}{\sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j (b_i + b_j)^3} \right)^{\frac{1}{\alpha}}
\]

(37)
The best value of $\alpha$ was determined to be unity. 

With the pseudo-criticals applicable to both liquid and vapor phases, it was possible to develop expressions for the equilibrium $K$ values,

$$K_i = \frac{y_i}{x_i}$$

where $y_i, x_i$ are the mole fractions of component $i$ in the vapor and liquid phases respectively. The resulting equation defining the $K$ value (for component 1) is

$$\ln (K_1) = \ln \frac{f_1}{f_G} + \left[ \psi_{1L} - \psi_{1G} \right]$$

where

$$\psi_{1L} = -\frac{1}{RT} \left( \frac{\hat{H}^* - \bar{H}}{T_c} \right) \left( \frac{\partial T_c'}{\partial x_1} - \sum_{i=1}^{n} x_i \frac{\partial T_c'}{\partial x_i} \right) - \left( \frac{z-1}{P_c'} \right) \left( \frac{\partial P_c'}{\partial x_1} - \sum_{i=1}^{n} x_i \frac{\partial P_c'}{\partial x_i} \right)$$

and

$$a_i = \left( \frac{z_c T_c}{P_c} \right)^{\frac{1}{2}}$$

$$b_1 = \frac{1}{2} \left( \frac{z_c T_c}{P_c} \right)^{1/3}$$

where

$$\ln \left( \frac{y_i}{x_i} \right) = T_c \left( \sum_{i=1}^{n} x_i \left( z_c \right)_i \right) \left( \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left( b_i + b_j \right) \right)^{3/2}$$
and \( \psi_{lg} \) is defined similarly for the vapor phase. Here, the fugacity \( f \), enthalpy \( (\tilde{H}^*-\tilde{H})/T_c' \), and compressibility \( z \) are the thermodynamic properties of the entire liquid or vapor phase. They may be determined for each phase with generalized charts or tables or by evaluating these properties from the known properties of a pure reference substance at the temperatures and pressure conditions \( T^0 \) and \( P^0 \), such that \( T^0 = (T_R')T_c^0 \) and \( P^0 = (P_R')(P_c^0) \) where \( T_c^0 \) and \( P_c^0 \) are the criticals of the reference substance chosen.

If the corresponding states principle were obeyed by all fluids exactly, it would make no difference which fluid was used as the reference. For the simple molecules which exhibit small deviations from corresponding states, and with a careful choice of the reference substance to be as similar as possible to the mixture, the \( K \)-values predicted by Equation (41) are in good agreement with experimental values\(^6\). To extend the applicability of the \( K \)-value calculation to mixtures comprised of molecules which have appreciable size and shape differences the size-shape factors for each component relative to the reference component must be introduced into the pseudo-critical expressions. The terms \( a_i \), \( b_i \), in (38) and (39) become with size-shape factors

\[
a_i = \left( \frac{(T_{ci}\Theta)^2 z_{ci}}{P_{ci} (\Theta/\phi)} \right)^{1/2} \tag{43}
\]
\[ b_i = \frac{1}{2} \left( \frac{T_{ci} Z_{ci}}{F_{ci}/\phi} \right)^{1/3} \]  

(44)

for both the liquid and vapor phases.
References


