L_p = length of straight pipe section
L = total length
N_{Re} = Reynolds number
m = proportionality constant
v = mean fluid velocity
μ_p = p^{th} moment about origin (dimensionless)
σ^2 = variance (dimensionless)
Δ = difference between outlet and inlet moments

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Note on the Use of Z_c as a Third Parameter with the Corresponding States Principle

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In a recent article by Reid and Leland (7), a brief comment about dimensional analysis was inserted on page 231 of the article with the statement that in a system described completely by the dimensional quantities P_c, V_c, T_c, R, P, V, T, the reduced equation of state relates the compressibility factor Z to only two independent dimensionless groups, implying that Z_c is not a variable. This statement is not correct and needs further explanation.

THE USE OF Z_c AS A THIRD PARAMETER

In empirical equations of state of the form

$$Z = f(P_R, T_R, Z_c, a_o, b_o, \ldots) \qquad (1)$$

where a_o, b_o, ... are dimensionless constants obtained by fitting PVT data which do not include the critical region, extrapolation of the equation to the critical will usually determine a constant Z_c, because the setting of $Z = Z_c$, $P_R = 1$, $T_R = 1$ in Equation (1) produces

$$Z_c = f(1, 1, Z_c, a_o, b_o, \ldots) \qquad (2)$$

which can be solved to give one or more constant roots for Z_c. The subscripts *o* indicate that these are universal constants applicable to all substances. However, if the critical region is included in the evaluation, the constants a_o, b_o, ... may be defined so that the values 1, 1, a_o, b_o, ... all cancel at the critical. The right side of Equation (2) then becomes only Z_c, so that the equation becomes the identity $Z_c = Z_c$ at the critical point. A method of doing this is to make three of the terms a_o, b_o, ... in Equation (1) not constants but variable universal functions of Z_c. These three terms are then defined by simultaneous solution of the equation of state with the required zero values of $(\partial P/\partial V)_T$ and $(\partial^2 P/\partial V^2)_T$ at the critical. This will define each as a function of Z_c. Substitution back into Equation (1) of all parameters defined in this way eliminates them from the equation by making them functions of Z_c. In this manner Equation (2) at the critical becomes

$$Z_c \equiv f[a_o(Z_c), b_o(Z_c), c_o(Z_c), \ldots d_o, e_o, \ldots] = Z_c \quad (3)$$

The functions $a_o(Z_c)$, $b_o(Z_c)$, $c_o(Z_c)$ will include the remaining constants d_o, e_o, ... in such a manner that they cancel at the critical and leave only Z_c on the right side of Equation (3). The equation thus becomes the identity $Z_c = Z_c$ (8).

The remaining universal constants d_o, e_o, ... can be present in any number to fit the compressibility at specific points away from the critical for various fluids. However, interpolations or extrapolations to other fluids not used to evaluate d_o, e_o, ... are determined in this case by a third parameter evaluated from the behavior of all fluids at their critical conditions. This interpolation or extrapolation to predict properties of other fluids is then assumed to be described at all conditions by the same third parameter which gives the correct interpolation at the critical. If a reduced equation with only three parameters could represent dissimilar fluids both at the critical and at low densities, this assumption would unquestionably be valid. Unfortunately, however, this is not the case. Any arbitrarily defined third parameter obtained at low densities and adjusted to fit virial coefficient data could be replaced by a function of Z_c if there is a smooth single-valued correlation of this parameter with Z_c. However, when Z_c is plotted against any third parameter which predicts low density PVT data, one obtains a scattering of points rather than a smooth curve. The higher members of the normal paraffin hydrocarbon series usually give the smoothest correlation. Hydrocarbons with other structures and other nonpolar molecules are usually scattered widely, so that two molecules with significant structural dissimilarities may have very nearly the same Z_c. Plots of this type are shown by Lydersen, Greenkorn, and Hougen (5) and by Hirschfelder et al (2).

The significance of this is that if one assumes the existence of a function

$$Z = f(T_R, P_R, Z_c) \qquad (4)$$

to allow interpolation in a table of experimental values of these reduced properties, one will obtain excellent results near the critical, but interpolations made away from the critical become more and more scattered as the density decreases. This increase in scatter at low densities has been pointed out by Hougen, Watson, and Ragatz (3). The obvious conclusion is that more than three parameters are needed to account for deviations from the simple corresponding states principle over extensive density ranges.

Hirschfelder et al. (2) use a four-parameter system involving both Z_c and the slope of the vapor pressure curve at the critical (Riedel's parameter) in addition to T_R and P_R.

The fact that more than one molecular parameter is needed has been shown clearly by Pople (6) in a theoretical discussion of the perturbation produced by nonsymmetrical molecular force fields on the simple two-parameter potential. A relatively simple form of deviation from the symmetrical force field of the two-parameter potential is that due only to nonsymmetrical dispersion forces when there are no permanent dipole moments. The first-order perturbation treatment developed by Pople (6) shows that the reduced second virial coefficient would require a four-parameter corresponding states representation, the dimensionless variables being

$$\frac{B}{\sigma^3} = f\left(\frac{\epsilon}{kT}, \kappa, \lambda\right) \tag{5}$$

The parameters σ and ϵ are, respectively, the separation distance at which the potential is zero and the negative of the minimum in the interaction potential. These two parameters alone would be sufficient if the molecular force field were spherically symmetric. There are two additional parameters introduced by the nonsymmetrical potential. The parameter κ is a dimensionless anisotropic polarizability factor defined as a ratio of terms involving the directional polarizability component parallel and perpendicular to a central molecular axis. The λ term accounts for shape effects important in molecular collisions. It is positive for rodlike molecules and negative for platelike molecules. Furthermore, it is entirely possible for a molecule with no permanent dipole moment to exhibit an appreciable quadrapole moment Θ, in which case another dimensionless group $\Phi^2/(\epsilon\sigma^5)$ must be added. The presence of permanent dipole moments introduces still more dimensionless variables. Thus, it is seen that even relatively slight deviations from the simple theory actually require more than three parameters to represent the low density region. The problem in using a three-parameter corresponding states principle is thus one of how best to optimize an approximate representation over the entire PVT range.

To obtain a three-parameter approximation for this simple case, one might neglect the λ term in the perturbation and consider only the κ term. This is equivalent to assuming the same contribution of all molecules to the repulsive part of the potential, regardless of their shape. Although this approximation might be satisfactory at low densities, it could hardly be expected to be valid at high densities and in the critical region. An exact fit at the critical with only these three parameters would require κ to be a smooth single-valued function of Z_c so that κ in the reduced equation might be replaced by $\kappa(Z_c)$ with the function chosen for $\kappa(Z_c)$ producing the identity $Z_c = Z_c$ at the critical. The actual correlation between κ and Z_c however is very poor.

COMPARISON OF Z_c WITH OTHER THIRD PARAMETERS

The use of any third parameter which is evaluated from PVT data may be regarded as the selection of a variable parameter to force the exact superposition of at least one point on a Z, P_R, T_R, or P_R, V_R, T_R diagram for all fluids with similar values of this parameter. Because of the identity at the critical, the use of Z_c forces this agreement at the critical point where there is relatively small variation in compressibility among fluids with appreciable differences in structure. The acentric factor, on the other hand, ensures that the reduced saturation pressure lines on all reduced diagrams with similar acentric factors merge at a reduced temperature of 0.7 and the best interpolations should lie in this region. As discussed above, if only three variable parameters could describe all fluids at all conditions so that the acentric factor could be expressed as a smooth single-valued function of Z_c, equally good results could be obtained by using either. In reality, plots of the acentric factor vs. Z_c show a great deal of scatter.

The use of either Riedel's parameter or Pitzer's acentric factor would ensure that the equation fits the data for all fluids exactly in a region below the critical on a PVT diagram. Consequently, there is much less scatter at lower densities. The region in which the best interpolations can be made among the different fluids lies below the critical density. Although there will, of course, be scatter in the equations of state at the critical point, this is usually less serious in view of the numerical closeness of Z_c for different fluids. Another advantage is that these other parameters are much more sensitive than Z_c to structural changes.

RELATION BETWEEN CORRESPONDING STATES AND DIMENSIONAL ANALYSIS

Although, as pointed out above, Z_c is not a very satisfactory parameter to account for corresponding states deviations at low densities, the ideal gas condition itself does not really restrict the dimensional analysis in the way the article states (7). The application of dimensional analysis to equations involving P_c, V_c, T_c, R, P, V, T is actually as follows. A typical equation of state in terms of these seven dimensioned quantities will contain groups of the form

$$(P^a V^b R^c T^d P_c^e V_c^f T_c^g) = \phi \tag{6}$$

where ϕ is defined as one of several dimensionless variables which appears in the equation of state function. With mass, length, time, and temperature (m, l, θ, t) used as dimensions, Equation (6) becomes

$$\left(\frac{m}{\theta^2 l}\right)^a (l^{3b}) \left(\frac{m\,l^2}{\theta^2 t}\right)^c t^d \left(\frac{m}{\theta^2 l}\right)^e (l^{3f})\, t^g = \phi \tag{7}$$

Dimensional homogeneity requires

$$\begin{aligned} \Sigma\, m &= 0 = \quad a + c + e \\ \Sigma\, \theta &= 0 = -2a - 2c - 2e \\ \Sigma\, t &= 0 = -c + d + g \\ \Sigma\, l &= 0 = -a + 3b + 2c + 3f - e \end{aligned} \tag{8}$$

Since the first two equations are identical, only three of the exponent unknowns can be eliminated. This is also shown by the rank of the matrix of the coefficients of these equations as shown in Figure 5 of the article (7). The exponents to be eliminated are chosen arbitrarily as

$$\begin{aligned} a &= -e - c \\ b &= -c - f \\ d &= -g + c \end{aligned} \tag{9}$$

If there are no other restrictions applicable to the exponents, Equation (9) produces four dimensionless groups in the general term. Substitution of Equation (9) into the exponents of Equation (6) produces

$$\left(\frac{PV}{RT}\right)^{-c} \left(\frac{P}{P_c}\right)^{-e} \left(\frac{V}{V_c}\right)^{-f} \left(\frac{T}{T_c}\right)^{-g} = \phi \tag{10}$$

showing four variable dimensionless groups.

In applying dimensional analysis in general, one must be sure that there are no additional restrictions which apply to the exponents that could add another equation to the group in Equation (8). The article stated erroneously that the relation of R, P, V, T at low pressures provides such a restriction and reduces the total number of variable groups from four to three. The only consequence of the ideal gas limit is to influence the values of the exponents in the various terms of the equation of state. It does not provide an additional relationship among them in every term. The observed increase in scatter of reduced properties of various fluids when correlated with Z_c at low densities cannot be explained by dimensional analysis.

SIGNIFICANCE FOR PSEUDO CRITICAL VALUES

As pointed out in the article (7), the theoretical basis for deriving pseudo criticals involves finding average force constants in the intermolecular potential function for a pure reference fluid which has properties similar to those of the mixture. The theory relates these average force parameters to the composition and force parameters of the individual constituents of the mixture. Furthermore, the usual theoretical basis for the terms accounting for unlike molecule interactions in the pseudo criticals is some modification of the Lorentz–Berthelot combination rules for the force constants.

However, it is advantageous in engineering applications to replace these force constants with criticals, since force constants are frequently unknown for many substances and require the specification of a particular intermolecular potential function for their evaluation. Thus, a more general result is produced by relating force constants to criticals to define pseudo criticals rather than pseudo or average force constants. For dissimilar molecules this replacement of force constants by criticals takes place as follows: The simplest reduced equation of state in terms of force constants which can account for deviations from the simple corresponding states theory is

$$Z = f\left(\frac{\epsilon}{kT}, \frac{V}{\sigma^3}, \frac{l}{\sigma}\right) \tag{11}$$

where l/σ represents some form of length–width ratio or some other dimensionless ratio of molecular parameters. Application of the critical derivatives plus the equation itself at the critical provides three equations which can relate any three of the dimensionless groups at the critical to the remaining group in Equation (11). For example at the critical point

$$\begin{aligned} \epsilon/kT_c &= f_1(l/\sigma) \\ V_c/\sigma^3 &= f_2(l/\sigma) \\ Z_c &= f_3(l/\sigma) \end{aligned} \tag{12}$$

The first two equations show the relation between force constants and criticals.

$$\begin{aligned} \epsilon &= k f_1 \left[(l/\sigma) \right] T_c \\ \sigma^3 &= 1/f_2 \left[(l/\sigma) \right] V_c \end{aligned} \tag{13}$$

Consequently, for molecules with structural dissimilarities, force constants are no longer proportional to critical conditions as they are when (l/σ) is not a variable. This means that the criticals which appear should be modified by a structurally dependent factor. In the case of a pure component treated by a three-parameter corresponding states treatment, this is not important, because any function $f\left(\frac{T}{f_1(l/\sigma)kT_c}, \frac{V}{[f_2(l/\sigma)]^{-1} V_c}, l/\sigma\right)$ can also be written as either a function of $\left(\frac{T}{T_c}, \frac{V}{V_c}, l/\sigma\right)$ or $f\left(\frac{T}{T_c}, \frac{V}{V_c}, Z_c\right)$. In the case of a mixture of dissimilar molecules, however, the modifiers of the criticals are required in the derivation of pseudo criticals from theories which define average force constants to represent a mixture. In proceeding from

$$\begin{aligned} \overline{\sigma}^3 &= \sum_i \sum_j x_i x_j \sigma_{ij}^3 \\ \overline{\sigma}^3 \overline{\epsilon} &= \sum_i \sum_j x_i x_j \sigma_{ij}^3 \epsilon_{ij} \end{aligned} \tag{14}$$

where $\overline{\sigma}$ and $\overline{\epsilon}$ are force parameters of a pure refrence substance which represents the mixture, as derived in the article, the introduction of criticals produces

$$\frac{V_c'}{f_2(l/\sigma)_{\text{ref.}}} = \Sigma \Sigma x_i x_j \left[\frac{V_c}{f_2(l/\sigma)} \right]_{ij}$$

$$\left[\frac{k f_1(l/\sigma)}{f_2(l/\sigma)} \right]_{\text{ref.}} (V_c' T_c') = \Sigma \Sigma x_i x_j \left[\frac{V_c}{f_2(l/\sigma)} \right]_{ij} [k f_1 (l/\sigma) T_c]_{ij} \tag{15}$$

The terms on the left are the properties of the pure reference which represents the mixture.

If one then uses the last equation in (12) then Equation (15) may be written equally well as

$$\psi_1 (V_c', Z_c') = \sum_i \sum_j x_i x_j \psi_1 (V_c, Z_c)_{ij}$$

$$\psi_2 (V_c', T_c', Z_c') = \sum_i \sum_j x_i x_j \psi_2 (T_c, V_c, Z_c)_{ij} \tag{16}$$

which is equivalent to the starting point of the Stewart–Burkhard–Voo equation. An additional equation or assumption is needed to define $(l/\sigma)_{\text{ref.}}$ or Z_c'. In this form, if Z_c is included as a variable in addition to T_c and V_c, the system could account somewhat for molecular structural dissimilarities, neglecting, of course, the inadequacies of Z_c as a third parameter. The statement of the S–B–V equations in the form of Equation (16) thus has a generality not fully made clear in reference *1*.

If, however, the functions in Equation (16) are written

$$\psi_1 (V_c, Z_c) = f(V_c) = \left(\frac{V_c}{R}\right) = \left(\frac{Z_c T_c}{P_c}\right) \propto \frac{T_c}{P_c}$$

$$\psi_2 (T_c, V_c, Z_c) = \left(\frac{T_c V_c}{R}\right) = \left(\frac{Z_c T_c^2}{P_c}\right) \propto \frac{T_c^2}{P_c} \tag{17}$$

so that the expressions used for ψ_1 and ψ_2 are equivalent to V_c/R and $T_c V_c/R$, then Z_c is either omitted or does not act as an additional independent third parameter in the equations defining T_c' and V_c', and according to the theory there is not a complete accounting for the molecular dissimilarities. Including a third parameter in the equations for T_c' and V_c' should improve the results but would greatly increase the complexity of the equations. Remarkably good results are obtained by omitting a third parameter from the T_c' and V_c' equations and accounting for corresponding states deviations by using reference properties of a pure component, equation of state, or table at a molal average value of the third parameter. The Z_c term could be used as a third parameter in this manner. Among the different rules discussed in the article (7), only the Prausnitz and Gunn procedure attempts to introduce a third parameter into the two equations used to define the pseudo criticals.

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