A Generalized Hard-sphere Augmented Virial Equation of State

A generalized equation of state is developed by combining a hard-sphere equation with a truncated virial equation and generalizing the reduced hard-sphere diameter as a function of reduced temperature and acentric factor. The new equation quantitatively agrees with Pitzer's table of compressibility factor over wide ranges of gas and vapor states and is always better than the truncated virial equation. Since the terms in the equation are physically meaningful it is capable of being improved systematically by including higher virial coefficients and by using hard-core equations of state for non-spherical cores. The equation is extended to mixtures with well-developed combination rules.

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SCOPE

The search for useful equations of state has been a continuing effort owing to the great utility of a good equation for the concise representation of volumetric behavior as well as the derived thermodynamic properties. Starting with van der Waals equation, improvement has been obtained in the past by adding terms to the equation to fit the observed empirical volumetric behavior of fluids. The use of added terms in the equation is however not an unmixed blessing. Extrapolation of the equation, even to a small extent from the range of conditions at which the fitting was obtained, becomes more uncertain. More importantly, the empirical constants associated with the added terms need to be predicted for mixtures, and the predictions become more uncertain as the added terms become more complex.

In this work, we depart from the route of adding terms to the van der Waals equation. Instead we make use of two results from rigorous molecular theory: the virial equation and the hard-sphere equation. The virial equation has been limited in practice to low densities, and the hard-sphere equation has been shown to be specially meaningful for high densities. These separate limitations are eliminated as the two equations are combined. In this work we develop the new equation obtained by combining the virial equation (truncated after the second virial) with the hard-sphere equation. The equation is generalized and expressed entirely in reduced variables.

CONCLUSIONS AND SIGNIFICANCE

The hard-sphere augmented second virial equation obtained in this work represents a definite improvement of the corresponding virial equation and can be recommended to replace it in engineering calculations. The new equation quantitatively reproduces Pitzer and co-workers' generalized correlations of thermodynamic properties at high temperatures ($T_r > 1.5$) for the entire reduced pressure range (up to $P_r = 9.0$). At $T_r \geqq 2.0$ the new equation agrees with Pitzer and co-workers' correlation of Z to within 1.0% for simple fluids, and within 1.5% for normal fluids with $\omega = 0.25$. At $T_r = 1.5$ the agreement is within 1.5% for the Z of simple fluids up to $P_r = 9.0$ and of normal fluids of $\omega = 0.25$ up to $P_r = 5.0$, and the agreement is within 3.5% for normal fluids of $\omega = 0.25$ up to $P_r = 9.0$.

The extension of the new equation to mixtures is straightforward and follows the well-known combining rules of the second virials and the hard-sphere diameters. Here is one of the real advantages of an equation that is firmly based on molecular theory. The predicted results are compared with data on mixtures, and good agreement is obtained at the gas conditions noted above.

The significance of this work is not limited to the improved result shown here. The present equation can be viewed as the first one of a class of equations obtained by combining a hard-core equation with a truncated virial equation. In the present development the hard-core is a hard sphere, and the virial equation is truncated after the second virial. The present equation is therefore the simplest in this class. We expect the future members in this class to be developed to progressively improve the quantitative representation of gas and vapor thermodynamic properties.

Because of the great utility of equations of state in the concise representation of equilibrium properties, the search for useful equations has been a continuing effort. The development of empirical equations was reviewed by Martin (1967). In this work we describe a new equation that is obtained by combining the virial equation with a hard-sphere equation. Both the latter equations are derived from fundamental theory. However, the virial equation has been practically restricted to low densities and the hard-

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sphere equations are meant for high densities. Systematic combinations of the two may lead to a quantitative description of all densities.

Fundamental fluid theory has come a long way toward elucidating the structure and the thermodynamic properties of assemblies of hard-spheres. Two equations of state were obtained from solution of the Percus and Yevick integral equation for hard-sphere assemblies by Thiele (1963) and Wertheim (1963). Of these the compressibility equation given below is worthy of special attention

$$Z = \frac{1 + \eta + \eta^2}{(1 - \eta)^3} \tag{1}$$

where

$$\eta = \frac{\pi}{6} \tilde{N} \sigma^3 \rho \tag{2}$$

and ρ is the molar density, σ the diameter, and Z the compressibility factor. The equation closely predicts computer generated Monte Carlo and molecular dynamics data, with deviations below 1 to 2% within the density range studied in this work. Reiss, Frisch, and Lebowitz (1959) adopted a different approach to the study of hard-sphere systems. Applying the theory of scaled particles to hard-spheres they obtained an equation of state identical to Equation (1). Subsequently Gibbons (1969) extended their results and obtained an equation of state of nonspherical hard cores which included Equation (1) as a special case. The following development will be based on Equation (1).

AUGMENTING THE VIRIAL EQUATION

The virial equation of state is a series expansion of the compressibility factor isotherm about the point of zero density,

$$Z = \sum_i B_i \rho^{i-1} \tag{3}$$

The summation starts with $i = 1$ corresponding to $B_1 = 1$, the ideal gas limit. The higher virial coefficients B_i with $i > 1$ are functions of temperature for each substance and are related to the potential energy function of intermolecular action by the cluster integrals of Ursell and Mayer. Unfortunately virials higher than the second ($i > 2$) are not generally known with accuracy for real fluids. As a consequence the practical utility of the virial equation of state has been largely limited to low densities with the use of virials up to B_2 only.

The series of Equation (3) may be replaced by a series for hard-spheres plus a series of deviation terms to account for real molecules being different from hard-spheres.

$$Z = \sum_i B_i^{\text{h.s.}} \rho^{i-1} + \sum_i (B_i - B_i^{\text{h.s.}}) \rho^{i-1} \tag{4}$$

The superscript h.s. denotes hard-spheres.

Haar and Shenker (1970, 1971) suggested that the virial series for hard spheres in Equation (4) be replaced with Equation (1).

$$Z = \frac{1 + \eta + \eta^2}{(1 - \eta)^3} \tag{5}$$

Haar and Shenker observed, on the basis of B_i's derived from the (6-12) Lennard-Jones potential, that the perturbation series converges rapidly. At temperatures above the critical only the second virial appreciably reflects the attractive forces; the higher virials effectively reflect the repulsive forces only. Since repulsive forces are contained in the hard-sphere equation of state, the perturbation series can be truncated after the second virial at temperatures not much above the critical. Equation (5) simplifies to

$$Z = \frac{1 + \eta + \eta^2}{(1 - \eta)^3} + (B_2 - B_2^{\text{h.s.}}) \rho \tag{6}$$

with

$$B_2^{\text{h.s.}} = \frac{2}{3} \pi \tilde{N} \sigma^3 \tag{7}$$

Haar and Shenker explored Equation (6) with a $(6 - m)$ Lennard-Jones potential joined to a hard-sphere core at the distance of zero energy. The hard-sphere diameter and the energy well depth were determined by fitting experimental values of B_2 and (dB_2/dT). The results were found to compare well with experimental Z values on argon and on nitrogen in the gaseous states up to high densities.

GENERALIZING THE AUGMENTED EQUATION

The favorable results obtained by Haar and Shenker are now re-expressed in generalized reduced form, and the needed generalized functions will be developed and described.

Since both η and $B_2^{\text{h.s.}}$ of Equation (6) are simply related to the volume of the hard spheres $\frac{\pi}{6} \tilde{N} \sigma^3$, we define a reduced hard core volume by

$$\alpha = \frac{\pi}{6} \tilde{N} \sigma^3 \rho_c \tag{8}$$

ρ_c is the critical density in moles/volume. Referring to Equation (2), we express η in terms of α by

$$\eta = \alpha \rho_r \tag{9}$$

where $\rho_r = \rho/\rho_c$. Referring to Equation (7), we express $B_2^{\text{h.s.}}$ in α by

$$B_2^{\text{h.s.}} = 4 \alpha/\rho_c \tag{10}$$

We re-express Equation (6) completely in reduced quantities,

$$Z = \frac{1 + \alpha\rho_r + \alpha^2\rho_r^2}{(1 - \alpha\rho_r)^3} + (B_r - 4\alpha)\rho_r \tag{11}$$

The reduced second virial coefficient B_r is defined to be $B_2\rho_c$ and B_2 is the second virial of real fluids. To calculate it in this work, we adopt the reduced state correlation of Pitzer and coworkers (1961)

$$B_r' \equiv \frac{B_2 p_c}{RT_c} = B_r Z_c = f_1(T_r) + \omega f_2(T_r) \tag{12}$$

Pitzer correlated f_1 and f_2 with the equations

$$f_1(T_r) = 0.1445 - 0.33/T_r - 0.1385/T_r^2 - 0.0121/T_r^3 \tag{13}$$

$$f_2(T_r) = 0.73 + 0.46/T_r - 0.5/T_r^2 - 0.097/T_r^3 - 0.0073/T_r^8 \tag{14}$$

Pitzer showed these equations to be useful from $T_r = 0.55$ up to very high values.

A reduced states function for α is now developed by fitting Equation (11) to the generalized correlation of Z developed by Pitzer and coworkers. For this purpose we postulate

$$\alpha = (\sqrt[3]{\alpha^{(0)}} + \omega \sqrt[3]{\alpha^{(1)}})^3 \tag{15}$$

and $\alpha^{(0)}$ and $\alpha^{(1)}$ are functions of T_r only. $\alpha^{(0)}$ stands for the reduced hard core volume of simple fluids for which $\omega = 0$. The cubic root of $\alpha^{(0)}$ is therefore a measure of the collision diameter σ of simple spherical molecules. Previous investigations suggest it to be a linear function of temperature, decreasing slightly as temperature increases. The cubic root of $\alpha^{(1)}$ measures the difference of the effective diameter of nonspherical molecules from that of the corresponding simple molecule. This difference is postulated to be linear in ω.

To determine $\alpha^{(0)}$ we refer to Pitzer's table of $Z^{(0)}$. At a fixed T_r and ρ_r we compute Z by Equation (11) for various assumed values of $\alpha^{(0)}$; the values of $\alpha^{(0)}$ that give rise to errors of ± 1% and ± 2% in calculated Z are recorded. We then proceed to the next ρ_r and repeat the search. The calculations are highly insensitive to α at low pressures, thus reflecting that Equation (11) asymptotically approaches the second virial equation $(1 + B\rho)$ as ρ approaches zero. The hard-sphere equation degenerates into $(1 + B^{h.s.}\rho)$ and α is cancelled from the equation under these conditions. Figure 1 shows that as pressure increases the upper and lower bounds of α for a specified error tend to converge, thus defining a narrow range of acceptable α values. The calculations become highly sensitive to α at high pressures, indicating the progressively higher relative importance of the hard sphere contribution at high densities.

Pitzer's table of $Z^{(0)}$ is probably accurate to 1 to 2%. It seems reasonable to look for a fitting of no worse than 2%. The range of acceptable α values within this error bound are established at a number of T_r of interest by repeating the procedure illustrated in Figure 1. At each T_r the search is carried up to a reduced pressure of 9 which is the limit of Pitzer's table. The best straight line is passed through the acceptable ranges at the T_r studied. This line is represented by the equation

$$\sqrt[3]{\alpha^{(0)}} = 0.556 - 0.023\ T_r \qquad (16)$$

The decrease in hard core diameter with increase in temperature agrees with previous results for simple molecules. The rate of decrease appears to be comparable to the *ZBH* perturbation theory (Haar and Shenker, 1971) and is greater.

The generalized equation of state for simple fluids that is obtained by computing α of Equation (11) according to Equation (16) is shown in Figure 2 at $T \geqq T_c$. Excellent agreement is obtained with Pitzer's generalized correlation at all low pressures and all high pressures regardless of temperature. In the intermediate pressure region agreement is also excellent at high temperatures with $T_r =$ 1.5 or above. The equation becomes less satisfactory in the intermediate pressure range as temperatures approach the critical. The true critical temperature is subcritical according to the equation.

The $\alpha^{(1)}$ function is determined by repeating the above procedure for normal fluids with $\omega = 0.5$. The result is approximated with two straight line segments described by the equations

$$\sqrt[3]{\alpha^{(1)}} = 0.020 \qquad \text{at} \quad T_r < 1.845 \qquad (17)$$

and

$$\sqrt[3]{\alpha^{(1)}} = 0.142\ T_r - 0.242 \qquad \text{at} \quad T_r > 1.845 \qquad (18)$$

At low temperatures $\alpha^{(1)}$ is essentially a constant. At high temperatures $\alpha^{(1)}$ increases slightly with temperature. Thus the complex molecules apparently increase in size as a result of intensified vibration and rotation. Our finding here is in agreement with that of Flory and coworkers (1964) regarding the core volume of *n*-alkane molecules. For simple fluids molecular vibration and rotation plays no part, and the effective molecular size decreases with increasing temperature as molecular collisions become more energetic, causing deeper penetration. This effect which is represented by Equation (16) also applies to complex molecules, resulting in some cancellation between Equations (16) and (18) for the complex molecules.

The equation of state obtained with the use of the complete α function of Equations (15) to (18) in Equation (11) is applicable to all normal fluids. Figure 3 shows this equation compared to Pitzer's correlation for a normal fluid with $\omega = 0.5$. This value of ω is higher than most substances of usual interest, and roughly corresponds to that

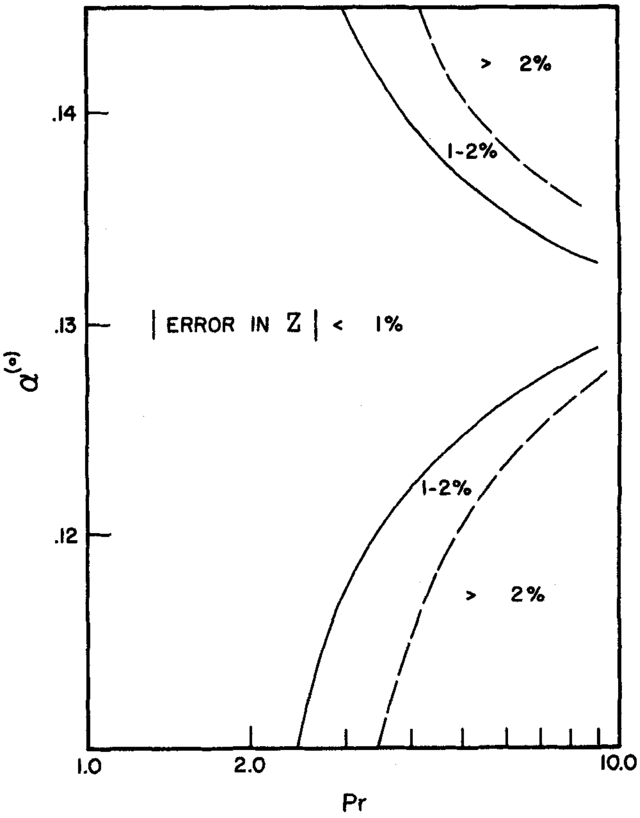

Fig. 1. Range of Alpha as a function of pressure at various error levels at $T_r = 2.0$.

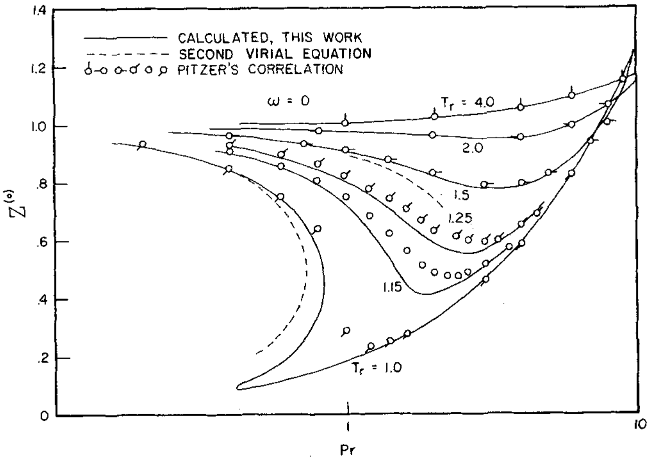

Fig. 2. Compressibility factor of simple fluids at $T_r \geqq 1.0$.

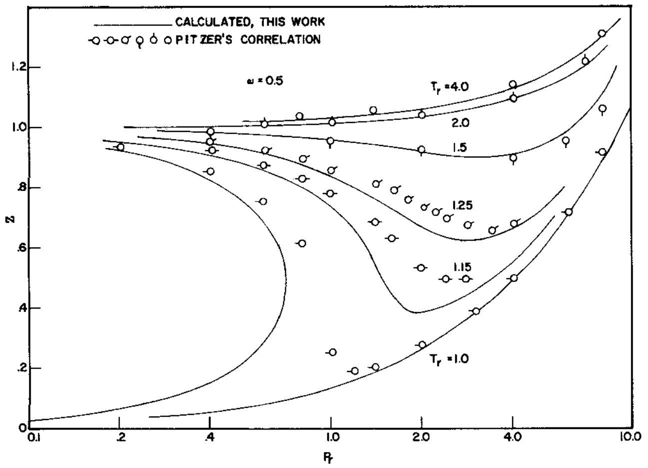

Fig. 3. Compressibility factors of normal fluids $\omega = 0.5$ at $T_r \geqq 1.0$.

of a C_{10} hydrocarbon. By using such a large value of ω we intend for the comparison in Figure 3 to bring out the differences of normal fluids from simple fluids. Our observations on simple fluids in connection with Figure 2 apply to the new comparison, except that the high pressure conditions are now less well represented at $T_r = 1.5$.

The generalization of the new equation of state is now complete. The use of the general equation for a specific substance requires four parameters to be known, namely, T_c, P_c, ρ_c, and ω. For normal fluids (Pitzer and Brewer, 1961) $Z_c = 0.291 - 0.080\ \omega$, leaving only three of these parameters to be independent.

The development of the α function is equivalent to the determination of a general expression of molecular diameter. The molecular diameter calculated from Equation (8) with our α function turns out to agree with accepted values. Figure 4 shows the literature value of Lennard-Jones collision diameter σ_{LJ} for n-hexane falls within the range of calculated σ of this work. Our α function was determined by considering behavior of high density fluids, while the Lennard-Jones collision diameters were obtained from studies of dilute gases. The agreement of results from such diverse sources confirms the validity of the theoretical considerations.

The effect of augmenting the second virial equation with the hard-sphere equation is shown in Figure 2 for $T_r =$ 1.0 and 1.5. The second virial equation agrees with the augmented equation and with Pitzer's generalized table values at low pressures. As pressure increases the second virial equation pulls away dramatically from the other two. Pitzer's generalized B_r', Equation (12), is used in the second virial equation. The comparison shows that augmenting the virial equation always leads to an improvement. The improvement increases as pressure or temperature or both are increased.

DERIVED THERMODYNAMIC FUNCTIONS

One of the most useful properties of equations of state is the concise representation of derived thermodynamic functions that is made possible with their use. In this section we examine the fugacity and enthalpy derived from the new generalized equation. These two properties are often of direct interest: fugacity in equilibrium considerations and enthalpy for heat balances. Algebraic combinations of fugacity, enthalpy, and molar volume in various manners produce numerous other derived functions, including entropy, Helmholtz free energy, etc. It is therefore unnecessary to directly examine these other functions here.

The derivation of a formula for calculating fugacity coefficient ($\phi = f/p$) starts with the following equation which is found in standard texts (Hirschfelder et al., 1954)

$$RT \ln \phi = \int_{\infty}^{V} \left[\frac{RT}{V} - \left(\frac{\partial p}{\partial n} \right)_{T,V} \right] dV - RT \ln Z \tag{19}$$

Upon substituting Equation (11) into (19) we obtain

$$\ln \phi = -\ln Z(1 - \alpha\rho_r) + 2(B_r - 4\,\alpha)\rho_r + 7y + 7.5y^2 + 3y^3 \tag{20}$$

where

$$y = \frac{\alpha\rho_r}{1 - \alpha\rho_r} \tag{21}$$

Figure 5 shows Equation (20) compared with Pitzer's correlation for simple fluids. Agreement appears to be very good in general. Deviations seem to be much less than that found in the Z-chart of Figure 1. Large deviations are not found in the neighborhood of the critical state, but substantial errors exist at higher pressures at the critical temperature and slightly above. This behavior is consistent with the fact that fugacity coefficient is an integral property and is related to the area enclosed by $Z = 1$ and the Z-isotherm of the equation. At $T_r \geqq 2.0$ the calculated ϕ agrees with Pitzer and coworkers' correlation to within 1.0% for simple fluids and normal fluids of $\omega = 0.25$ for the entire reduced pressure range (up to $P_r = 9.0$). At $T_r = 1.5$ the agreement is within 1.5% for simple fluids and within 3.5% for normal fluids with $\omega = 0.25$ for P_r up to 9.0.

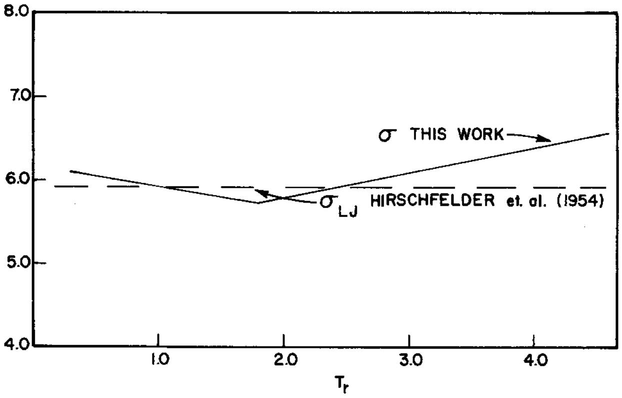

Fig. 4. Collision diameter of n-hexane.

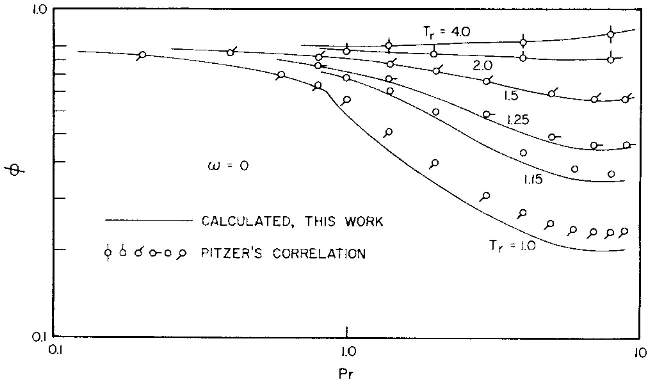

Fig. 5. Generalized fugacity coefficient for simple fluids.

The derivation of the enthalpy deviation function is based on the following general equation which is found in standard texts

$$H - H^* = \int_{\infty}^{V} \left[T\left(\frac{\partial p}{\partial T}\right)_V - p \right] dV + p\tilde{V} - RT \tag{22}$$

Upon substituting Equation (11) into (22) we obtain

$$\frac{H - H^*}{RT_c} = T_r^2 \left(\frac{d\alpha}{dT_r}\right)\left(\frac{1}{\alpha}\right) \left[1 - \frac{1}{1 - \alpha\rho_r} + \frac{3}{(1 - \alpha\rho_r)^2} - \frac{3}{(1 - \alpha\rho_r)^3}\right] + 4\rho_r\left(\frac{d\alpha}{dT_r}\right) T_r^2 - \frac{dB_r}{dT_r}\rho_r T_r^2 + (Z - 1)T_r \tag{23}$$

Figure 6 shows the enthalpy function calculated from Equation (23) in comparison with Pitzer's generalized correlation for simple fluids. Good agreement appears to have been obtained except for high pressures at the critical temperature or slightly above.

EXTENSION TO MIXTURES

Equations of state are extended to mixtures with the use of mixing rules. The present equation of state sets itself apart from the empirical equations in this extension. The mixing rules for the present equation are not arbitrary but well defined because the parameters of the equation have precise physical significance. Thus the combining rule for the second virial coefficient is rigorously given by Ursell and Mayer's cluster theory; and the collision diameter for unlike hard spheres is the arithmetic average of the corresponding like pairs.

Extension of the present equation to mixtures requires the equation of state of hard-sphere mixtures be known. Several such equations have been proposed that will reduce into Equation (1) for the special case of the spheres being all of the same size. We have adopted in this work the following equation as the basis for extension to mixtures,

$$Z = \frac{1}{1 - \eta} + \frac{(4\pi\rho)^2 (\sum_i R_i^2 x_i)^3}{3(1 - \eta)^3} + \frac{4\pi\rho(\sum_i R_i^2 x_i)(\sum_i R_i x_i)}{(1 - \eta)^2} \tag{24}$$

where

$$\eta = \frac{4\pi}{3}\tilde{N}\rho\,(\sum_i R_i^3 x_i) \tag{25}$$

x_i are the mole fractions and R_i the collision radii. Equation (24) has been obtained from scaled-particle theory of hard-sphere mixtures and from solution of the Percus-Yevick equation (Lebowitz, 1964). Gibbons' general equation for similar hard-cores of arbitrary shape (Gibbons, 1969) reduces to Equation (24) for the special case of spherical cores.

Mansoori, Carnahan, Starling, and Leland (1971) proposed an improved equation of state (MCSL equation) for hard sphere mixtures. We made some calculations according to Equation (24) for comparison with MCSL equation and with computer generated data by Monte Carlo calculations. The results are shown in Table 1 in the density range of interest in this work. The entries for MCSL equation and for the Monte Carlo data in the table are taken from Mansoori et al. (1971). The comparisons show MCSL equation to be in excellent agreement with Monte Carlo data. The two equations show maximum differences of about 1% at pressures of up to about 200

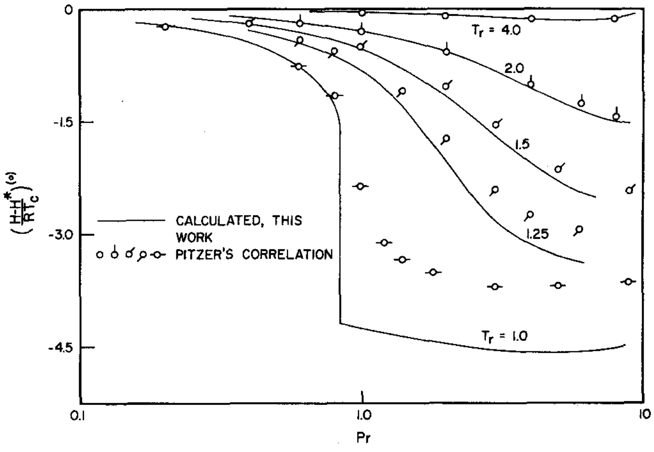

Fig. 6. Generalized enthalpy deviation function for simple fluids.

Table 1. Comparison of the Compressibility Factor Z for a Binary Mixture of Hard Spheres ($x_1 = x_2 = .5$) with the Monte Carlo (MC) Data

η	0.1571	0.2618	0.3665
Pressure of methane at the ice point, atm. (approximately)	135.0	200.0	600.0
$R_2/R_1 = 1.1$			
Mansoori et al.	1.963	3.253	5.688
Equation (24)	1.96	3.29	5.88
MC	1.96	3.17	5.64
$R_2/R_1 = 5/3$			
Mansoori et al.	1.879	3.041	5.214
Equation (24)	1.88	3.07	5.37
MC	1.87	3.04	5.24

η	0.2333	0.2692	0.3106	0.3583	0.3808
Pressure of methane at the ice point, atm. (approximately)	200.0	270.0	340.0	550.0	
$R_2/R_1 = 3$					
Mansoori et al.	2.368	2.772	3.356	4.241	4.764
Equation (24)	2.38	2.80	3.41	4.35	4.91
MC	2.37	2.77	3.36	4.24	4.76

to 270 atmospheres for all the molecular size ratios studied. The largest differences between the equations amount to about 3% and are found at the maximum pressures studied. Equation (24) is adopted because it is potentially the most generally applicable through Gibbons' extension of it to arbitrary hard cores and because it closely approximates the Monte Carlo data.

The second virial coefficient of an assembly of hard spheres derived from Equation (24) is

$$B^{\text{h.s.}} = \frac{2\pi}{3} \sum_i \sum_j (R_i + R_j)^3 \, x_i x_j \qquad (26)$$

A hard-sphere-augmented virial equation for mixtures is obtained upon combining Equation (24) with Equation (26),

$$Z = \frac{1}{1-\eta} + \frac{(4\pi\rho)^2 \, (\Sigma\, R_i^2 x_i)^3}{3(1-\eta)^3} + \frac{4\pi\rho (\Sigma\, R_i^2 x_i)(\Sigma\, R_i x_i)}{(1-\eta)^2}$$
$$+ \sum_i \sum_j x_i x_j \left[\tilde{V}_{cij} \, B_{rij} - \frac{2\pi}{3} (R_i + R_j)^3 \right] \rho \qquad (27)$$

As before the hard-sphere radii $R_i = \sigma_i/2$ are given by Equation (8) and the generalized α function. Mixing rules required in connection with the second virial coefficients have been extensively investigated (Chueh and Prausnitz, 1967). We adopt the following:

$$\tilde{V}_{cij} = (\tilde{V}_{ci}^{1/3} + \tilde{V}_{cj}^{1/3})^3/8 \qquad (28)$$

$$T_{cij} = (1 - k_{ij})(T_{ci} T_{cj})^{1/2} \qquad (29)$$

B'_{rij} is then given by Equation (12). In this development k_{ij} is the only new parameter introduced for the extension of the equation of state to mixtures. In the calculations described below k_{ij} are taken from Chueh and Prausnitz (1967) unless otherwise indicated. Regardless of the value of k_{ij}, Equation (27) reduces to Equation (11) for pure substances.

Volumetric properties are calculated from Equation (27) for comparison with experimental data for a number of systems. Figure 7 shows the comparison for methane/carbon dioxide at 280°F. With $k_{12} = 0.05$ the calculations are in good agreement with the data of Reamer et al. (1944). Figure 8 shows the compressibility factor of methane/hydrogen sulfide mixtures at 220°F. With $k_{12} = 0.05$ the calculations are in good agreement with Sage and Lacey's data (1955) except for the 2000 lb./sq.in.abs. point of high H_2S concentration. The deviations are apparently related to the proximity to the critical region of H_2S for which $T_c = 212°F$.

Figure 9 shows the compressibility factors of nitrogen/n-butane mixtures for which the calculations are made with $k_{12} = 0.12$. The agreement with Evans and Watson's data (1956) seems excellent for mixtures high in nitrogen but become less satisfactory as the concentration of n-butane increases. The temperature of the mixtures is only about 5°C above the T_c of n-butane.

The fugacity of components in gas mixtures are important in equilibrium calculations. The fugacity coefficient ϕ_N ($= f_N/x_N p$) can be derived from equations of state according to the general formula

$$RT \ln \phi_N = \int_\infty^V \left[\frac{RT}{V} - \left(\frac{\partial p}{\partial n_N} \right)_{T,V,n_j} \right] dV - RT \ln Z \qquad (30)$$

Upon substituting Equation (27) into (30), we obtain the working formula

$$\ln \phi_N = -\ln(1 - C\rho) + \frac{(2C + A + D)\rho}{1 - C\rho} + \frac{(C^2 + AC + B + 2CD + DE)\rho^2}{2(1 - C\rho)^2}$$

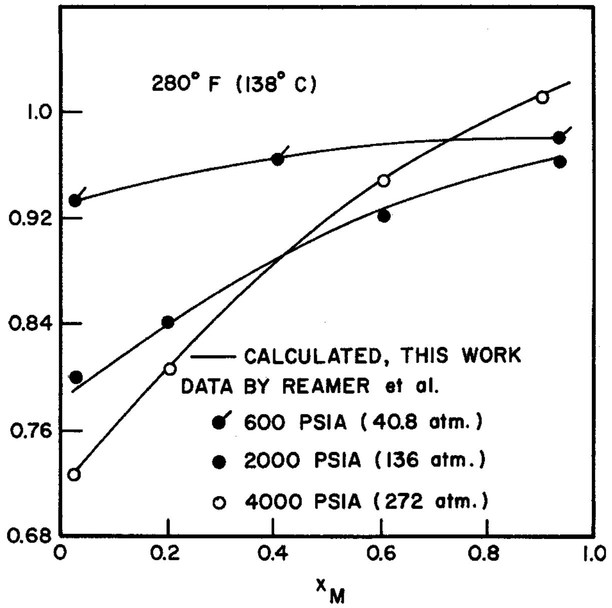

Fig. 7. Z of methane/carbon dioxide mixtures at 280°F.

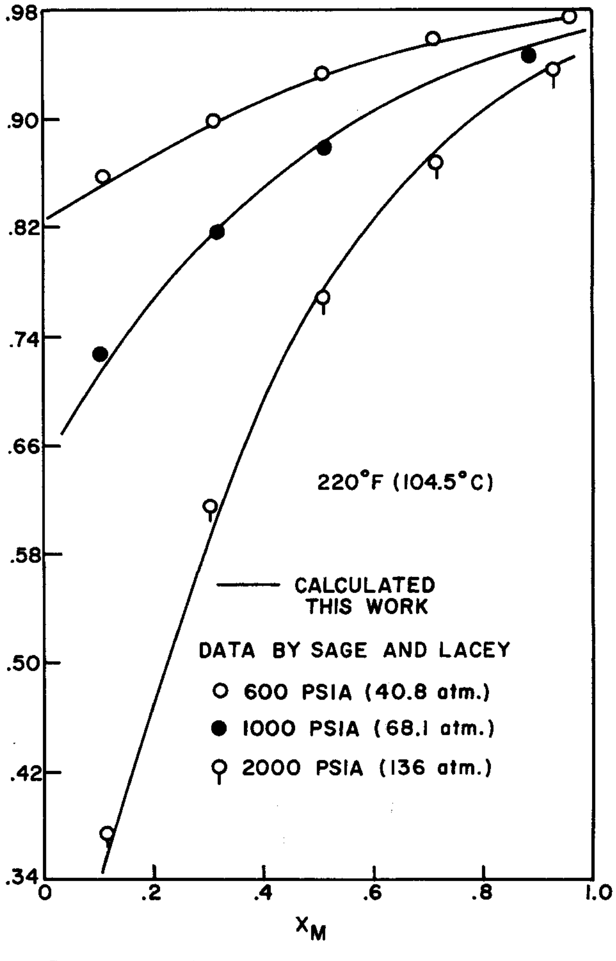

Fig. 8. Z of methane/hydrogen sulfide mixtures at 220°F.

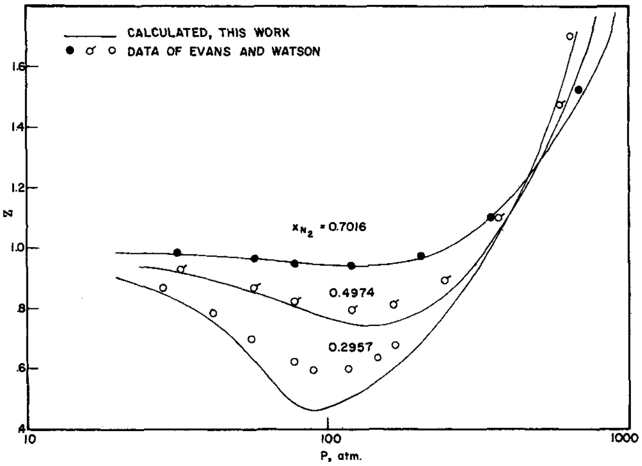

Fig. 9. Z of nitrogen/n-butane mixtures at 310°F.

$$+ \frac{(C^2D + CDE + DF)\rho^3}{3(1 - C\rho)^3} + G\rho - \ln Z \quad (31)$$

where

$$\tilde{A}/\tilde{N} = 4\pi R_N^2 \sum_i R_i x_i + 4\pi R_N \sum R_i^2 x_i - \frac{8\pi}{3} (R_N^3 + \sum_i x_i R_i^3) \quad (32)$$

$$B/\tilde{N} = 16\pi^2 R_N^6 x_N^2 + \frac{32}{9}\pi^2 R_N^6 x_N + \frac{16}{9}\pi^2 \sum (R_i^3 x_i)^2 - \frac{16\pi}{3} \sum_i \sum_j x_i x_j \,(R_N^3 R_i R_j^2 + R_N^2 R_i R_j^3 + R_N R_i^2 R_j^3) \quad (33)$$

$$C/\tilde{N} = \frac{4}{3}\pi \sum R_i^3 x_i \quad (34)$$

$$D/\tilde{N} = 4\,\pi\, R_N^3 \quad (35)$$

$$E/\tilde{N} = \frac{4\pi}{3} \sum_i \sum_j x_i x_j (R_i + R_j)^3 \quad (36)$$

$$F/\tilde{N}^2 = \frac{16\pi^2}{3} (\sum_i R_i^2 x_i)^3 + \frac{16\pi^2}{9} (\sum_i R_i^3 x_i)^2 - \frac{16\pi^2}{3} (\sum_i \sum_j \sum_k R_i R_j^2 R_k^3 x_i x_j x_k) \quad (37)$$

$$G = 2 \sum_i \tilde{V}_{ciN}\, B_{riN}\, x_i - \frac{4\pi}{3} \tilde{N} \sum_i x_i (R_i + R_N)^3 \quad (38)$$

The algebraic combinations appear complicated, but calculations are straightforward on computers.

ACKNOWLEDGMENT

This work was supported on National Science Foundation Grant GK-4023.

NOTATION

B = second virial coefficient
H = enthalpy
k = binary interaction constant
$\tilde{N}$ = Avogadro's number
P = pressure
R = gas constant
= molecular radius
T = absolute temperature
V = volume
x = mole fraction
Z = compressibility factor

Greek Letters

α = reduced volume of hard-spheres
ρ = density
σ = molecular diameter
ϕ = fugacity coefficient
ω = acentric factor

Subscripts

c = critical property
r = reduced property

Superscripts

(0) = simple fluids
(1) = function that expresses deviation from simple fluid behavior
$*$ = ideal gas

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Manuscript received May 8, 1972; revision received August 15, 1972; paper accepted September 13, 1972.