

## **Equation of State for Mixtures of Nonpolar Fluids: Prediction from Experimental Constants of the Components**

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We present a simple procedure by which an analytical equations of state for a mixture of normal fluids can be predicted from the constants  $T_c$  (critical temperature),  $p_c$  (critical pressure), and  $\omega$  (Pitzer acentric factor) for each pure component. The equation covers the range from the dilute vapor or gas to the highly compressed liquid or supercritical fluid.

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**KEY WORDS:** equation of state; gases; mixtures; nonpolar fluids.

### **1. INTRODUCTION**

An accurate analytical equation of state for mixtures of nonpolar molecular fluids, based on statistical-mechanical perturbation theory, was recently proposed by Ihm et al. [1], who also showed how the equation could be used with varying amounts of input information. The maximum information, at present available only for the noble gases, consists of all the intermolecular potentials plus one constant used to describe each pure dense fluid. In the absence of knowledge of the intermolecular potentials, an optimal amount of information consists of the second virial coefficients as functions of temperature, including the interaction coefficients, plus one constant for each pure dense fluid. The least information needed at present is the second virial coefficient of each pure component as a function of temperature, plus one constant for each pure dense fluid.

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The purpose of this paper is to show how the Ihm-Song-Mason equation of state [1] can be used with even less input information. In particular, knowledge of only three constants is sufficient to determine the  $p$ - $v$ - $T$  surface of a pure normal fluid with an accuracy of a few percent; the equation of state of the mixture can then be found straightforwardly, as shown by Ihm et al. [1]. The three constants are the critical temperature ( $T_c$ ), the critical pressure ( $p_c$ ), and the Pitzer acentric factor ( $\omega$ ). The latter constant can be obtained from a single measurement of the vapor pressure. These three constants are available for a large number of substances [2, 3].

Our essential contribution here is to show how the temperature-dependent parameters of the statistical-mechanical equation of state can be predicted from the constants  $T_c$ ,  $p_c$ , and  $\omega$  with little loss of accuracy. We first describe this procedure and then test it on 33 nonpolar substances having a variety of molecular structures. Finally, we summarize how the mixture equation of state is to be obtained from these results.

## 2. PROCEDURE

The equation of state that is the basis of this work is, for a single fluid [4],

$$\frac{p}{\rho kT} = 1 + \frac{(B - \alpha)\rho}{1 + \delta b\rho} + \frac{\alpha\rho}{1 - \lambda b\rho} \quad (1)$$

where  $p$  is the pressure,  $\rho$  is the number density,  $kT$  has its usual meaning,  $B(T)$  is the second virial coefficient,  $\alpha(T)$  and  $b(T)$  are two parameters that depend only on the molecular repulsive forces, and  $\delta$  and  $\lambda$  are constants. The term  $\delta b\rho$  is a small correction, and  $\delta$  can be taken equal to  $0.22\lambda$ . The constant  $\lambda$  is determined experimentally from a few high-density points, such as liquid densities. Because  $\alpha(T)$  and  $b(T)$  are insensitive to the detailed shape of the intermolecular potential, they can be calculated if  $B(T)$  is known experimentally, by means of some effective mean-spherical potential [4-6]. The results of such calculations are conveniently recorded as the dimensionless quantities  $\alpha/v_B$  and  $b/v_B$ , which are almost-universal functions of the dimensionless temperature  $T/T_B$ . Here the scale factors  $T_B$  and  $v_B$  are the Boyle temperature, at which  $B=0$ , and the Boyle volume,  $v_B \equiv T_B(dB/dT)_{T_B}$ . The critical constants  $T_c$  and  $v_c$  are not suitable as scale factors because analytical equations of state cannot be trusted to give an accurate description of the region around the critical point, which is known to be nonanalytic.

The minimum input information needed to determine the equation of state thus consists of experimental values of  $B(T)$  and  $\lambda$  for each pure

component. We now show how this input information can be obtained from the constants  $T_c$ ,  $p_c$ , and  $\omega$ .

It is clear that  $B(T)$  plays a central role in the present equation of state. Not only is it used directly, but it is also the source of the Boyle constants used to find  $\alpha(T)$  and  $b(T)$ . There are several correlations by which  $B(T)$  can be estimated from the values of  $T_c$ ,  $p_c$ , and  $\omega$  [3, 7, 8]; we have used the expression

$$(p_c/RT_c)B = f^{(0)}(T_r) + \omega f^{(1)}(T_r) \quad (2)$$

where  $T_r = T/T_c$  and the group  $RT_c/p_c$  serves as a pseudocritical volume. The functions  $f^{(0)}$  and  $f^{(1)}$  are

$$f^{(0)}(T_r) = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8} \quad (3)$$

$$f^{(1)}(T_r) = 0.0637 + \frac{0.331}{T_r^2} - \frac{0.423}{T_r^3} - \frac{0.008}{T_r^8} \quad (4)$$

Not only does this correlation furnish values of  $B(T)$ , but also it supplies good estimates of  $T_B$  and  $v_B$ , needed to find  $\alpha(T)$  and  $b(T)$ . The virtue of this result is that  $\alpha(T)$  and  $b(T)$  can be found from the critical constants without contaminating the entire  $p$ - $v$ - $T$  surface with the nonanalytic difficulties of the critical region. The values of  $T_B$  and  $v_B$  calculated numerically from Eqs. (2)–(4) can be accurately represented by the expressions

$$T_B/T_c = 2.6455 - 1.1941\omega \quad (5)$$

$$v_B(p_c/RT_c) = 0.1646 + 0.1014\omega \quad (6)$$

Agreement with known experimental values of  $T_B$  and  $v_B$  is usually within a few percent, which is adequate because any errors will automatically be compensated by the choice of the constant  $\lambda$ , as described below. Once  $T_B$  and  $v_B$  are known,  $\alpha(T)$  and  $b(T)$  can easily be calculated from available tables based on an effective (12, 6) potential model [5] or from empirical equations fitted to those tables [9, 10].

To determine the value of the constant  $\lambda$  at least one high-density  $p$ - $v$ - $T$  result is needed. For consistency, to find  $\lambda$  we have used the density of the saturated liquid at a temperature of  $T_r \approx 0.7$ , which is the temperature at which the acentric factor  $\omega$  is usually determined. Once this is done, the entire volumetric behavior of the given fluid is established.

### 3. RESULTS

We have chosen 33 normal fluids having a variety of structural types for testing the present prediction scheme. An important criterion for selection was the existence of a large amount of reliable  $p$ - $v$ - $T$  data. The fluids can be classified into the following six groups for convenience:

Noble gases: Ne, Ar, Kr, Xe

Diatomics: N<sub>2</sub>, O<sub>2</sub>, CO, Cl<sub>2</sub>

Inorganic polyatomics: CO<sub>2</sub>, N<sub>2</sub>O, SO<sub>2</sub>, BF<sub>3</sub>, NF<sub>3</sub>, CF<sub>4</sub>, SF<sub>6</sub>

C<sub>1</sub>-C<sub>4</sub> alkanes: CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, *n*-C<sub>4</sub>H<sub>10</sub>

C<sub>5</sub>-C<sub>8</sub> alkanes: *n*-C<sub>5</sub>H<sub>12</sub>, four hexanes, *n*-C<sub>7</sub>H<sub>16</sub>, *n*-C<sub>8</sub>H<sub>18</sub>

Other hydrocarbons: C<sub>2</sub>H<sub>4</sub>, propene, butene-1, propyne, benzene, toluene

We exhibit the experimental data as graphs of  $G^{-1}$  vs  $b\rho$ , where  $G(b\rho)$  is

$$G(b\rho) \equiv \frac{1}{\alpha\rho} \left[ Z - 1 + \frac{(\alpha - B)\rho}{1 + \delta b\rho} \right] \quad (7)$$

in which  $Z \equiv p/\rho kT$  is the compression factor. According to Eq. (1), this is a straight line of slope  $-\lambda$ . The theoretical significance of  $G(b\rho)$  is that it is the effective average pair distribution function for equivalent hard bodies at contact [4, 6]. A critical sampling of typical results is shown in Fig. 1,

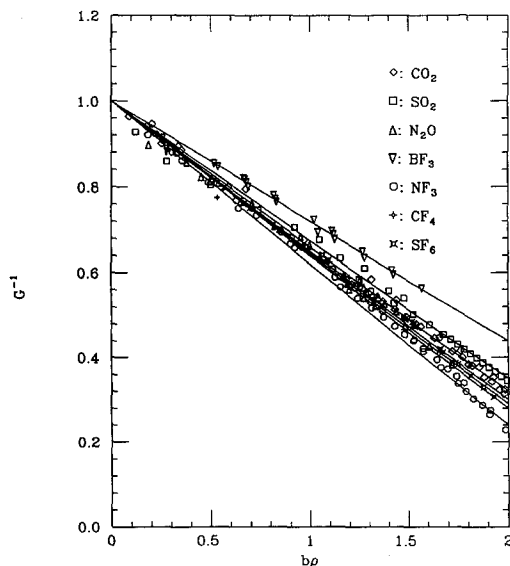


Fig. 1. Typical plots of  $G^{-1}$  vs  $b\rho$ , where  $G(b\rho)$  is given by Eq. (7).

representing the inorganic polyatomic gases. The results for the other five groups are similar, as shown by deviation plots.

Deviation plots for the above six groups are shown in Fig. 2, where  $\% \text{ Dev.} \equiv 100(\rho_{\text{calc}} - \rho_{\text{exp}})/\rho_{\text{exp}}$ . The deviations are mostly under 2% for the noble gases and gradually increase to mostly under 5% as the molecular structure becomes more complex. This is not surprising, since the underlying theory is based on a perturbation treatment of the statistical mechanics for fluids of hard convex bodies [4, 6].

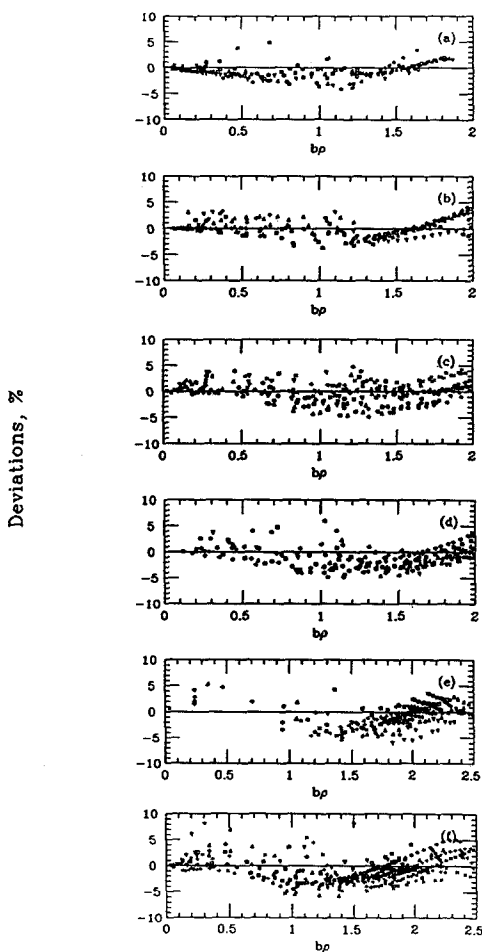


Fig. 2. Deviation plots for various systems: (a) noble gases, (b) diatomics, (c) inorganic polyatomics, (d)  $C_1$ - $C_4$  alkanes, (e)  $C_5$ - $C_8$  alkanes, and (f) unsaturated and aromatic hydrocarbons.

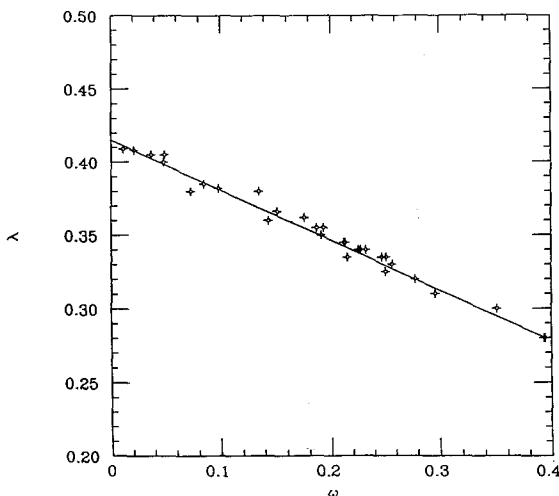


Fig. 3. Correlation of the empirical constant  $\lambda$  with the acentric factor  $\omega$ . The straight line is given by Eq. (8).

An important result is that the values of  $\lambda$ , which were determined from saturated liquid densities at about  $0.7 T_c$ , correlate quite closely with the values of  $\omega$ , as shown in Fig. 3. The correlation is represented by the linear relation,

$$\lambda = 0.4146 - 0.3164\omega \quad (8)$$

We believe that most of the scatter shown in Fig. 3 arises from deviations in the calculated values of  $B(T)$ ,  $T_B$ , and  $v_B$ , which are reflected in compensating variations in  $\lambda$ .

Thus the entire volumetric behavior of a fluid can be calculated analytically from just the values of  $T_c$ ,  $p_c$ , and  $\omega$ .

#### 4. MIXTURES

There is no need to repeat the formulas for the mixture equation of state, since they are available [1]. Here we only summarize how the foregoing results are to be used to generate the mixture results. The only mixture quantities needed are the temperature-dependent pairwise interaction parameters  $B_{ij}(T)$ ,  $\alpha_{ij}(T)$ , and  $b_{ij}(T)$ . For these we use, in principle, effective mean-spherical potentials, although these do not actually need to enter explicitly into the calculations. The potential well-depth parameter  $\epsilon$

is proportional to  $T_B$ , and the well-position parameter  $r_m$  is proportional to  $v_B^{1/3}$ . The simplest combining rules are thus

$$T_{Bij} = (T_{Bi}T_{Bj})^{1/2} \quad (9)$$

$$v_{Bij}^{1/3} = \frac{1}{2}(v_{Bi}^{1/3} + v_{Bj}^{1/3}) \quad (10)$$

More accurate combining rules are available [11] and should be used if possible, but they require knowledge of the polarizabilities and dispersion coefficients of the pure substances in order to calculate corrections to Eqs. (9) and (10).

Once  $T_{Bij}$  and  $v_{Bij}$  are known, the values of  $\alpha_{ij}(T)$  and  $b_{ij}(T)$  are calculated as for the pure components.

To find  $B_{ij}(T)$  we must know  $T_{cij}$ ,  $(p_c/RT_c)_{ij}$ , and  $\omega_{ij}$ . A simple arithmetic mean seems to be adequate for  $\omega_{ij}$  [12],

$$\omega_{ij} = \frac{1}{2}(\omega_i + \omega_j) \quad (11)$$

The value of  $T_{cij}$  then follows from  $T_{Bij}$  and  $\omega_{ij}$  according to Eq. (5), and the value of  $(p_c/RT_c)_{ij}$  follows from  $v_{Bij}$  and  $\omega_{ij}$  according to Eq. (6). Then  $B_{ij}(T)$  follows from Eqs. (2)–(4) in the same as for the pure components. This completes the determination of the mixture equation of state.

As an example, we have calculated the equation of state for  $\text{CO}_2 + \text{C}_2\text{H}_6$  mixtures according to the foregoing procedure. The results are essentially indistinguishable from those obtained by Ihm et al. [1].

## 5. CONCLUSIONS

This work demonstrates that the entire  $p$ - $v$ - $T$  surface of a normal nonpolar fluid can be constructed with reasonable accuracy from just the three constants  $T_c$ ,  $p_c$ , and  $\omega$ . The volumetric behavior of a mixture of any number of normal components can then be constructed according to the procedure of Ihm et al. [1], with only the use of combining rules for potential parameters.

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