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Thermophysical Properties from the Equation of State of Mason and Co-workers[1]

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The theory gives formulas for calculating the three temperature-dependent parameters of the equation of state from the intermolecular potential. But the second virial coefficient also serves to predict the entire equation of state in terms of two scaling parameters and, hence, a number of other thermodynamic properties including the Joule–Thomson inversion curve, bulk modulus, secant bulk modulus, and inverse isobaric expansivity among others. Agreement with experimental data is quite good.

KEY WORDS: bulk modulus; equation of state; inverse isobaric expansivity; Joule–Thomson inversion curve; secant bulk modulus.

1. INTRODUCTION

The influence of attractive intermolecular forces can be treated by statistical–mechanical perturbation theory, as can the softness of repulsions. Given the intermolecular potential, it is possible to predict the thermodynamic properties of molecular fluids. Three integrations are needed, one to find the second virial coefficient, one to find a scaling factor, and one to find an effective hard-sphere diameter. The equation is usable with much less input than the full intermolecular potential, since the scaling factor and the effective diameter are nearly universal functions when expressed in suitable reduced units.

Knowledge of the second virial coefficient as a function of temperature enables one to predict the entire equation of state (EOS), as shown by Ihm et al. [1]. In addition, one temperature-independent constant that is the characteristic of the particular substance is needed. In the present work,

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this EOS derived by Ihm, Song, and Mason (ISM) is used to find selected thermophysical properties of fluids, and the results are compared with experimental values.

2. THEORETICAL CONSIDERATION

We consider the statistical-mechanical equation of state derived by Song and Mason [2], which is based on the Week–Chandler–Anderson (WCA) perturbation theory for the condensed state. The derivation begins with the equation relating the pressure to the pair distribution function, $g(r)$,

$$\frac{P}{\rho kT} = 1 - \left(\frac{2\pi\rho}{3kT}\right) \int_0^\infty \left(\frac{\partial u}{\partial r}\right) g(r)\, r^3\, dr \tag{1}$$

where ρ is the density, P is the pressure, kT is the thermal energy per molecule, and $\partial u/\partial r$ is the derivative of the intermolecular potential function with respect to the distance r. Upon applying the perturbation scheme of the WCA method to the potential function and working out a correction, for attractive forces, the equation of state reads [1]

$$\frac{P}{\rho RT} = 1 + \frac{(B-\alpha)\rho}{1+0.22\lambda b\rho} + \alpha\rho G(b\rho) \tag{2}$$

where the new corresponding-states principle has the form

$$G(b\rho)^{-1} = \alpha\rho\left[Z - 1 + \frac{(\alpha - B)\rho}{(1+0.22\lambda b\rho)}\right]^{-1} \approx (1-\lambda b\rho) \tag{3}$$

and $Z = P/\rho RT$ is the compressibility factor. Here $G(b\rho)$ is the average pair distribution function at contact for equivalent hard convex bodies that still have pairwise additivity of the intermolecular forces. The many-body nature of the system may be contained in $G(b\rho)$. λ is the magnitude of the slope of G^{-1} vs $b\rho$, a constant that must be determined empirically. λ is shown to incorporate quantum effects [3].

The parameters B, α, and b are related to the intermolecular potential, u, by integrations and are defined as follows:

$$B(T) = 2\pi \int_0^\infty (1 - e^{-u/kT})\, r^2\, dr \tag{4}$$

$$\alpha(T) = 2\pi \int_0^{r_m} (1 - e^{-u_0/kT})\, r^2\, dr \tag{5}$$

$$b = \alpha + T\frac{d\alpha}{dT} \tag{6}$$

where u_0 is the repulsive part of u and r_m is the position of minimum in u. However, $B(T)$ can be found experimentally, and $\alpha(T)$ and $b(T)$ can be calculated from $B(T)$ by means of simple two-constant scaling rules [4]. The reason is that b and α depend only on the intermolecular repulsive forces and are therefore relatively insensitive to the details of the shape of the intermolecular potential; they can be characterized by two constants corresponding to an average potential strength and range.

3. COMPARISON WITH EXPERIMENTAL DATA

The equation of state is related by rigorous thermodynamic expressions to many equilibrium properties, which can be used as tests. In this section we give a selection of such tests. These include the Joule–Thomson inversion curve, bulk modulus, secant bulk modulus, and inverse isobaric expansivity.

3.1. Joule–Thomson Inversion Curve

The Joule–Thomson inversion curve is a sensitive test of the EOS [5]. The Joule–Thomson coefficient is related to the equation of state by the thermodynamic formula

$$\mu_{JT} = \frac{T(\partial V/\partial T)_p - V}{C_p} \tag{7}$$

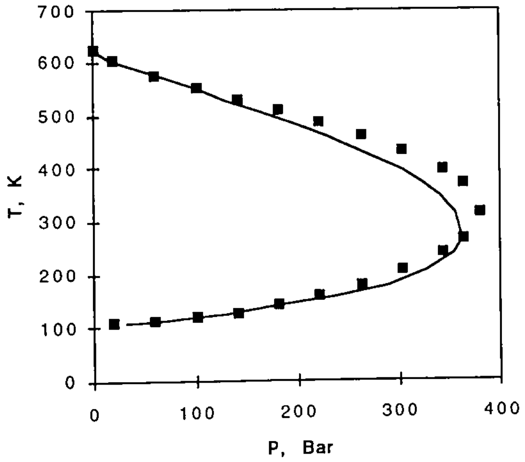

Fig. 1. The curve is calculated from the present equation of state, Eq. (8), and the points are experimental data for nitrogen [7].

where C_p is the specific heat capacity at constant pressure. The inversion curve is determined by the condition $\mu_{JT}=0$; for the present equation of state this yields

$$\frac{T(dB/dT)-B-(T(d\alpha/dT)-\alpha)}{1+0.22\lambda b\rho}+\frac{T(d\alpha/dT)-\alpha}{1-\lambda b\rho}$$
$$+\frac{0.22\lambda(B-\alpha)(b-T(db/dT))}{(1+0.22\lambda b\rho)^2}\rho+\frac{\alpha\lambda(T(db/dT)-b)}{(1-\lambda b\rho)^2}\rho=0 \qquad (8)$$

If ρ is eliminated between Eqs. (2) and (8), the inversion pressure may be obtained in terms of the inversion temperature. Analytical elimination of ρ is not straightforward, but it is easy to proceed numerically. The curve calculated from Eq. (8), with smoothed values of $B(T)$ from Ref. 6, is compared with experimental points for nitrogen [7]. The results are shown in Fig. 1.

3.2. Bulk Modulus

The reduced bulk modulus is defined as

$$\bar{B}=\rho\left(\frac{\partial P}{\partial \rho}\right)_T \Big/ RT\rho_B \qquad (9)$$

where ρ_B is Boyle's density.

The linear temperature dependence of the reduced bulk modulus for each isochore has been investigated using an equation of state based on

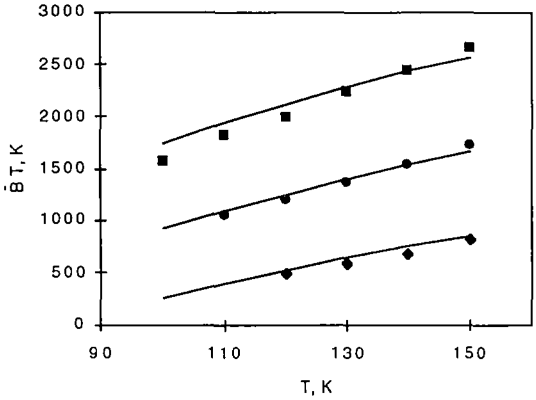

Fig. 2. The calculated and experimental values of the bulk modulus divided by $R\rho_B$ of Ar at $\rho=28$ (◆), $\rho=30$ (●), and $\rho=33$ (■) mol · L^{-1}. The line was calculated from Eq. (2), and the symbols are experimental values.

statistical mechanical theory (ISM EOS) for Ar. The result is in good agreement with reliable experimental data [8]. The values of $\alpha(T)$ and $b(T)$ for pure Ar can be calculated using Table 1 of Ref. 1. We have used the experimental values of the second virial coefficient for Ar [6]. The results are shown in Fig. 2.

3.3. Secant Bulk Modulus

The secant bulk modulus is defined as

$$\mathbf{B}=\frac{V_0(P-P_0)}{V_0-V}=\frac{P-P_0}{1-\rho_0/\rho} \tag{10}$$

where V_0 and P_0 are reference volume and reference pressure, respectively. **B** corresponds to the slope of the secant cutting the compression curve. The linear relationship between the secant bulk modulus and the temperature at constant density can be obtained for molecular liquids by using Eq. (2). The generalization of Eq. (2) to mixtures of any number of components takes the form [9]

$$\frac{P}{\rho RT}=1+\rho\sum_{ij}x_ix_j(B_{ij}-\alpha_{ij}F_{ij})+\rho\sum_{ij}x_ix_j\alpha_{ij}G_{ij} \tag{11}$$

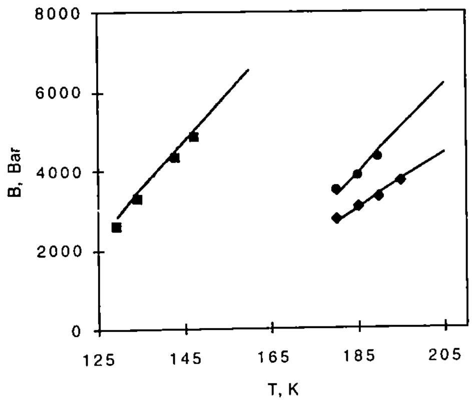

Fig. 3. The calculated and experimental values of the secant bulk modulus of liquid Kr at 26.667 mol · L^{-1} (◆) [12], a 0.556 Kr + 0.444 Xe liquid mixture at 25 mol · L^{-1} (●) [12], and a 0.485 Ar + 0.515 Kr liquid mixture at 31.746 mol · L^{-1} (■) [13]. The lines were calculated from Eqs. (2) and Eq. (11) for Kr and mixtures, respectively. The symbols are experimental values.

where x_i and x_j are mole fractions, and the summations run over all components of the mixture. The quantities α_{ij} and B_{ij} are related to the pair potential $u_{ij}(r)$. G_{ij} and F_{ij} are defined in Ref. 9.

We now compare the theoretical results from these equations of state with experimental data for Kr as a molecular liquid, and for Kr–Xe and Ar–Kr as liquid mixtures. We have used the HFD-C potential given by Aziz and co-workers [10, 11], for obtaining the values of B_{ij}, b_{ij}, and α_{ij} for Kr–Xe and Ar–Kr. The results are shown in Fig. 3, where the agreement between calculated and experimental values is remarkably good. The values of V_0 (L mol^{-1}) and P_0 (bar) used in Fig. 3 for Kr, Kr–Xe, and Ar–Kr are (0.0446, 37.4), (0.0453, 61.0), and (0.0366, 135.8), respectively.

3.4. Inverse Isobaric Expansivity

The isobaric expansivity $\alpha = (\partial V/\partial T)_P/V$ can be calculated from Eqs. (2) and (11) for Ar and Ar–Kr mixture respectively. The resultant equations are too complicated to give the physical interpretation. But it is easy to proceed numerically. We have performed such calculations over a wide range of pressure and temperatures The results are shown in Figs. 4 and 5. We have used the best available intermolecular potentials of the HFD-C form given by Aziz and co-workers [11] for Ar–Kr. Figure 4 shows the isochores of $1/\alpha$ vs. P for Ar. A typical isochores is shown for Ar–Kr in Fig. 5. This regularity provides a significant constraint on equations of state.

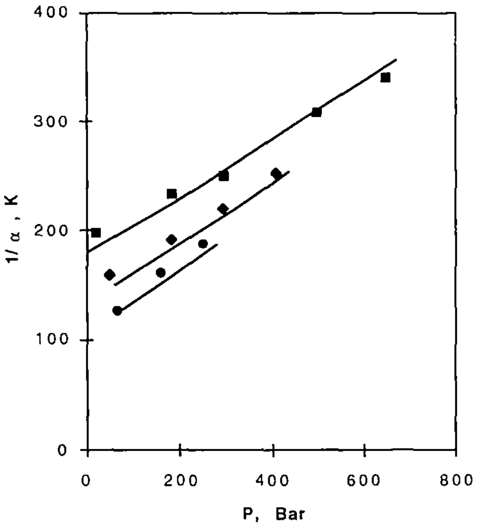

Fig. 4. Inverse isobaric expansivity versus pressure for argon isochores at $\rho = 28$ (●), $\rho = 30$ (◆), and $\rho = 33$ (■) mol · L^{-1} [7].

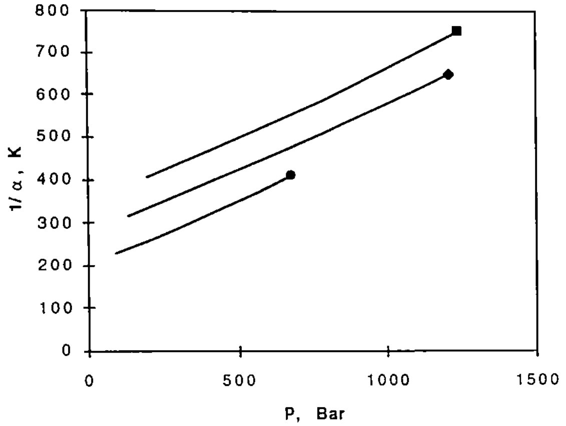

Fig. 5. Same as Fig. 4 for 0.485 Ar + 0.515 Kr isochores at $\rho = 29$ (●), $\rho = 32$ (◆), and $\rho = 34$ (■) mol · L^{-1}.

4. CONCLUSION

The Joule–Thomson inversion curve seems to be reasonable and insensitive to the model used for b and α. A new regularity of the reduced and secant bulk modulus as a function of temperature has been found for the ISM EOS. The regularity holds for Ar and Kr as well as Kr–Xe and Ar–Kr mixtures, while the isochores of $1/\alpha$ vs P provides a constraint on EOS. Finally, our present work (ISM EOS) compared to Ref. 14 (LIR EOS) indicates that a more reliable Joule–Thomson inversion curve can be obtained. In addition, the regularities have been extended to fluid mixtures.

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