



A Few Thermo-physical Properties of Inert Fluids (Ar, Kr, Xe And Ar-Kr, Kr-Xe) from a Simple Equation of State

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ABSTRACT

The used simple equation of state formula contains three temperature dependent parameters viz.: Second virial coefficient, an effective hard convex bodies (HCB'S) diameter, and scaling factor for pair distribution function at contact. All the parameters can be calculated from the intermolecular potential of HCB'S, and hence the thermodynamic properties such as Joule-Thomson inversion curve, bulk modulus, and isobaric expansivity etc., are calculated. The agreement of these calculated data with experimental data is quite good.

Key words: Joule-Thomson inversion curve, Bulk modulus, Isobaric expansivity, Hard convex bodies, Intermolecular potential.

1. INTRODUCTION

A central problem in the theory of fluids is the extension of their thermodynamic parameters in terms of intermolecular forces. One of the fundamental approaches to this problem is through the formulation of an accurate equation of state (EOS), since the thermodynamic functions can be easily derived once the EOS is known. Recent works by Song and Mason [1] on a statistical mechanical theory for the EOS of fluids have yielded simple but accurate results for molecular fluids. Three temperature dependent parameters arise in their formulation; second virial coefficient, an effective HCB'S diameter, and a scaling factor for pair distribution function at contact. All of the parameters can be calculated from the intermolecular potential. For a given intermolecular potential for hard convex bodies (HCB's) [2-6] it is also possible to predict the thermodynamic properties of molecular fluids such as Joule-Thomson inversion curve, bulk modulus etc., The influence of attractive intermolecular forces can be treated by statistical mechanical perturbation theory, as can the softness of repulsions. Both isotropic and orientational correlations exhibit simpler behavior in the surface-to-surface than in the more customary center-to-center co-ordinate representation. All the intermolecular forces in the HCB model are transmitted perpendicularly to the surface, the natural co-ordinates are derived from the surface normal

(or apse vector) and the shortest surface-to-surface separation [3-18]. Conventionally, center-to-center distances (plus orientations) have been employed to express intermolecular properties of atomic fluids. By means of support function, all the geometric properties of the HCB can be derived. In this work, this EOS is used to find selected thermodynamic properties of fluids, and the results are compared with experimental values. The advantage of this study is that one can equally predict the thermo-physical properties of these inert fluids and their mixtures by taking the ratio of semi major-axis and semi minor-axis to a constant value i.e., by incorporating shape factor of the molecule into account. Agreement with experiment was excellent for these fluids.

2. MATHEMATICAL MODEL

The Lennard-Jones (L J) potential which has pair-wise additive property can be used to approximately describe the intermolecular interactions.

$$\phi = 4E \left[\left(\frac{h(x)}{K} \right)^p - \left(\frac{h(x)}{K} \right)^q \right] \quad (1)$$

Where K is an intermolecular distance, E is the energy for the intermolecular distance at which the potential disappears. p and q respectively is the exponent of the repulsive and the attractive terms. At higher densities,

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the thermodynamic properties of liquid are chiefly governed by an intermolecular potential but mainly determined by its repulsive term.

The HCB [2-6] with semi major-axis m and semi minor-axis n, the support function is

$$h(x) = n \left[1 + \varepsilon x^2 \right]^{\frac{1}{2}} \quad (2)$$

Where $x = \hat{K} \cdot \hat{e} = \cos \theta$, $\varepsilon = \left(\frac{m}{n} \right)^2 - 1$ and $\frac{m}{n} = 2$

Where \hat{K} is the surface normal or apse vector and \hat{e} is the orientation vector. The pair potential for HCB is characterized by three constant parameters m, n, and E. We have obtained the value of E from the available experimental data [19]. The potential well minimum occurs at $K = \frac{1}{2^6} h(x)$. We consider the

statistical-mechanical EOS derived by Song and Mason [1], which is based on the Week-Chandler-Anderson (WCA) perturbation theory for the condensed state. The derivation of the Song and Mason EOS begins with the equation relating the pressure to the pair distribution function, g(r).

$$\frac{P}{\rho R T} = 1 - \left(\frac{2 \pi \rho}{3 k T} \right) \int_0^\infty \left(\frac{\partial u}{\partial r} \right) g(r) r^3 dr \quad (3)$$

Where ρ is the density, P is the pressure, kT is the thermal energy per molecule, and $\frac{\partial u}{\partial r}$ is the derivative

of the intermolecular potential function with respect to the distance r. On applying the perturbation scheme of the WCA method to the potential function and working out a correction for attractive forces, the EOS reads [20].

$$\frac{P}{\rho R T} - \alpha \rho G(b \rho) = 1 + \frac{(B_2 - \alpha) \rho}{1 + 0.22 \lambda b \rho} \quad (4)$$

Where the new corresponding-states principle has the form

$$G(b \rho) = \alpha \rho \left[Z - 1 + \frac{(\alpha - B_2) \rho}{1 + 0.22 \lambda b \rho} \right] \approx \frac{1}{(1 - \lambda b \rho)} \quad (5)$$

And $Z = \frac{P}{\rho R T}$ is the compressibility factor. Here,

$G(b \rho)$ is the average pair distribution at contact for equivalent HCB 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} versus $b \rho$ a constant

that must be determined empirically. λ is shown to incorporate quantum effects [21-23]. The product λb is analogous to the Van der Waals excluded volume. The second virial coefficient B_2 in terms of center-to-center (r, θ, φ) [4].

Coordinate system may be written as

$$B_2(T) = \frac{N}{4} \iiint \left[1 - e^{\frac{-u}{kT}} \right] dr^3 \quad (6)$$

The virial coefficient described for center-to-center (r, θ, φ) coordinate system has been expressed in terms of surface-to-surface (K, θ, φ) coordinate system and angles measured with respect to normal \hat{K} or apse vector specifying minimum surface-to-surface distance. The full Jacobian for the transformation from center-to-center to surface-to-surface coordinate system [5] is

$$dr^3 = \left[\left(\frac{\partial r}{\partial \theta} \times \frac{\partial r}{\partial \phi} \right) \cdot \hat{K} \right] d\theta d\phi dK \quad (7)$$

$$= S(x, K) d\theta d\phi dK B_2(T) = \frac{N}{4} \int_0^\infty \int_0^\pi \int_0^{2\pi} \left(1 - e^{-\frac{u}{KT}} \right) \quad (8)$$

$$\left[\begin{aligned} & K^2 + \frac{2Kn^2}{h(x)} + \frac{n^4}{h^2(x)} + \frac{\varepsilon Kn^4}{h^3(x)} \\ & + \frac{\varepsilon Kn^4 x^2}{h^3(x)} + \frac{\varepsilon n^6}{h^4(x)} - \frac{\varepsilon x^2 n^6}{h^4(x)} \\ & + \frac{\varepsilon^2 n^8}{4h^6(x)} \sin^2 \varphi - \frac{\varepsilon^2 x^2 n^8}{2h^6(x)} \sin^2 \varphi \\ & + \frac{\varepsilon^2 x^2 n^8}{4h^6(x)} \sin^2 \varphi \end{aligned} \right] (d\theta d\phi dK)$$

Where $\theta = \pi$, $\varphi = 2\pi$ are respectively, the polar and azimuthal angles. The weight function S(x, K) for each value of the surface-to-surface distance K is Jacobian determinant. The parameters α and b are related to the intermolecular potential u_0

$$\text{by } \alpha(T) = \frac{N}{4} \iiint \left[1 - e^{\frac{-u_0}{kT}} \right] S(x, K) d\theta d\phi dK \quad (9)$$

$$b = \alpha + T \frac{d\alpha}{dT} \quad (10)$$

Where u_0 is the repulsive part of u and surface-to-surface distance K is the position of the potential well minimum.

The value of $B_2(T)$ can be calculated using equation (6) for any ratio of m and n and for a known value of E . The calculation of these temperature dependent parameters $a(T)$ and $b(T)$, are performed via their scaling rules and LJ potential [24]. The reason is that b and a 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 EOS can be used as sensitive tests thermophysical properties. These include the Joule-Thomson inversion curve and bulk modulus and isobaric expansivity.

3.1. Joule-Thomson Inversion Curve

The Joule-Thomson inversion curve is a sensitive test of the EOS [24]. The Joule-Thomson coefficient is related to the EOS by the thermodynamical formula

$$\mu_{JT} = \frac{1}{C_p} \times \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] \quad (11)$$

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 EOS this yields

$$\begin{aligned} & \frac{T \left(\frac{dB_2}{dT} \right) - B_2 - \left(T \left(\frac{da}{dT} \right) - a \right)}{1 + 0.22 \lambda b \rho} + \frac{T \left(\frac{da}{dT} \right) - a}{1 - \lambda b \rho} + \\ & \frac{0.22 \lambda (B_2 - a) \left(b - T \left(\frac{db}{dT} \right) \right)}{(1 + 0.22 \lambda b \rho)^2} \rho \\ & + \frac{a \lambda \left(T \left(\frac{db}{dT} \right) - b \right)}{(1 - \lambda b \rho)^2} \rho = 0 \end{aligned} \quad (12)$$

If ρ is eliminated between equations (4) and (12), the inversion pressure may be obtained in terms of the inversion temperature. Analytical of ρ is not straightforward, but it is easy to proceed numerically. The curve calculated from equation (12), with smoothed values of $B(T)$ from Ref. [22], is compared with experimental points for nitrogen [25]. The results are shown in Figure 1. From this figure, the maximum pressure is found to be 376 atmospheres falling at temperature 313.15 K. In the group of substances (air, O_2 , Ar, CH_4 , CO) whose critical temperature are above that of nitrogen the upper branch of the inversion curve falls largely or completely above our temperature range. In the group of substances (Ne, H_2 , He) whose critical temperature fall below that of

nitrogen, the lower branch of inversion curve falls completely below our temperature range. Agreement with experimental data is quite good.

3.2. Bulk Modulus

The reduced bulk modulus is defined as

$$\bar{B} = \frac{1}{RT \rho_B} \times \left[\rho \left(\frac{\partial P}{\partial \rho} \right)_T \right] \quad (13)$$

Where ρ_B is Boyle's density.

The linear temperature dependence of the reduced bulk modulus for each isochore has been investigated using an EOS based on statistical mechanics theory for Ar. The result is in good agreement with reliable experimental data [26]. The values of $a(T)$ and $b(T)$ for pure Ar are taken [20]. We have used the experimental values of the second virial coefficient for Ar [27]. The results are shown in Figure 2.

3.3. Isobaric Expansivity

The expansivity $\alpha = \frac{1}{V} \left[\left(\frac{\partial V}{\partial T} \right)_p \right]$ can be calculated from equation (4) and from the generalized equation

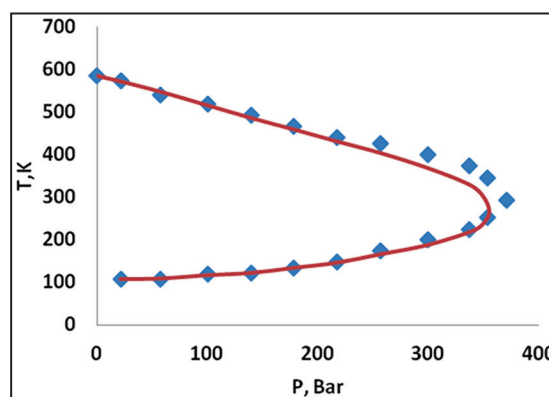


Figure 1: The curve is calculated from the present equation of state, equation (11), and the points are experimental data for nitrogen [25].

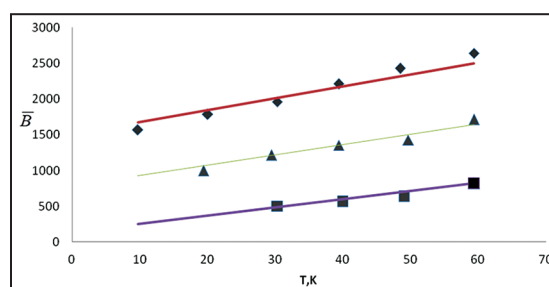


Figure 2: The calculated and experimental values of the bulk modulus divided by $R\rho_B$ of Ar at $\rho = 28$ (■), $\rho = 30$ (▲), and $\rho = 33$ (◆) mol.L^{-1} . The line was calculated from equation (4) and the symbols are experimental values.

of equation (4). The generalization of equation (4) to mixtures of any number of components takes the form [7].

$$\frac{P}{\rho R T} = 1 + \rho \sum_{ij} x_i x_j (B_{ij} - \alpha_{ij} F_{ij}) + \rho \sum_{ij} x_i x_j \alpha_{ij} G_{ij} \quad (14)$$

This equation is solved numerically to find the physical interpretation. We have performed such calculations over a wide range of temperatures and pressures. The results are shown in Figures 3 and 4. Figure 3 shows the isochores of $1/\alpha$ versus P for Ar. A typical isochore is shown for Ar-Kr in Figure 4. This regularity provides a significant constraint on EOS the.

4. CONCLUSION

The Joule–Thomson inversion curve seems to be reasonable and insensitive to the model used for

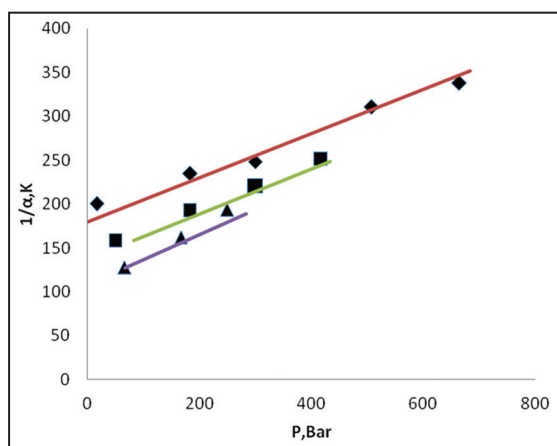


Figure 3: Isobaric expansivity versus pressure for argon isochors at $\rho = 28$ (\blacktriangle), $\rho = 28$ (\blacksquare) and $\rho = 33$ (\blacklozenge) mol. L^{-1} .

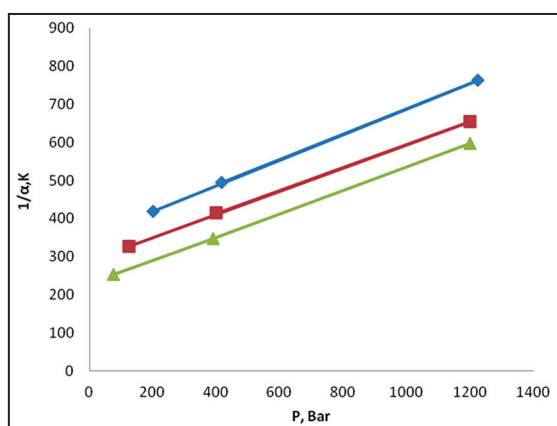


Figure 4: Same as Figure 3 for 0.485 Ar + 0.515 Kr isochores at $\rho = 29$ (\blacktriangle), $\rho = 32$ (\blacksquare) and $\rho = 34$ (\blacklozenge) mol. L^{-1} .

b and α . Furthermore, we may safely conclude that the parameters of the potential fit the experimental values of the second virial coefficient of HCB'S. The regularity holds for Ar and Kr as well as Kr-Xe and Ar-Kr mixtures while the isochores of $1/\alpha$ versus P provides a constraint on EOS. Furthermore, the regularities have been extended to the fluid mixture. Our work does not indicate a great advantage of the K-based (surface-to-surface) over the r-based (center-to-center) representation. This concludes that taking shape factor of the molecule into account that is by taking the different ratio of major and minor axis does not improve the quality of prediction. However, this work is good on mathematical modeling of physical chemistry, especially in the thermodynamic field. In addition, the methodology proposed in this paper provides a new tool of further calculation of other thermodynamic properties.

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***Bibliographical Sketch**



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