An Equation of State for Argon

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Abstract

An analytical equation of state was applied to calculate the thermodynamic properties for argon. The equation of state is that of Song and Mason. It is based on a statistical-mechanical perturbation theory of the hard convex bodies and can be written as fifth-order polynomial in the density. There exist three temperature-dependent parameters: the second virial coefficient, an effective molecular volume, and a scaling factor for the average contact pair distribution function of hard convex bodies. We used Lennard-Jones (12-6) potential for calculation of temperature-dependent parameters. The equation of state has been applied to calculate thermodynamic properties including the vapor pressure curve, the compressibility factor, fugacity coefficient for argon. The agreement with experiment is good.

1. Introduction

Since the discovery of argon in 1893, this substance has been the subject of numerous experimental and theoretical investigations. Due to the widespread use of argon in both scientific and industrial applications, there is special interest in its thermodynamic properties. The chemically inert behavior and the low market price resulting from its large occurrence in air (about 0.934% by volume) predestine argon for the generation of protective atmospheres in industrial

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applications, e.g., as an inert-gas shield for arc welding and cutting or as a blanket for the production of titanium and other reactive elements.

From a thermodynamic point of view the great importance of argon lies in its molecular simplicity. Since the molecule is monoatomic, nonpolar and completely spherical, argon is commonly used as a reference fluid to establish and test molecular approaches for the prediction of thermodynamic properties and for the calibration of new apparatuses for thermodynamic measurements.

For all these applications, knowledge of the thermodynamic properties of argon is an important precondition. An earlier compilation of the thermodynamic properties of argon is the international table edited and compiled by Angus et al. [1]. This book was published in 1972 and is based on the compilation by Gosman, McCarty, and Hust [2], published in 1969, and the compilations by Vasserman, and Rabinovich [3], and by Vasserman, Kazavchinskii, and Rabinovich [4], published in 1968 and 1966, respectively.

The correlation by Stewart et al. [5], published in 1982, utilized a fundamental equation based upon selected data, some of which were published after the previous correlations has been completed.

A central problem in the theory of fluids is the relation 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, since the thermodynamic functions can be easily derived once the equation of state is known. The most successful theories at present are perturbation theories based on reference systems consisting of hard bodies [6] analogous to the perturbation theories of simple fluids based on hard spheres. Recent work by Song and Mason on a statistical-mechanical theory for the equation of state of fluids has yielded simple but remarkably accurate results for both spherical [7] and molecular [8] fluids. Three temperature-dependent parameters arise in their formulation: the second virial coefficient, an effective hard-sphere diameter, and a scaling factor for the pair distribution function at contact. All three parameter can be calculated from the intermolecular potential. The purpose of this work is to apply this equation of state to calculate thermodynamic properties of argon.

2. Theory

Song and Mason [8] obtained an analytical equation of state for convex-molecule fluids based on statistical-mechanical perturbation theory. The equation of state is of the form,

$$\frac{P}{\rho kT} = 1 + B_2(T)\rho + \alpha(T)\rho[G(\eta) - 1] \quad (1)$$

where P is the pressure, ρ is the molar (number) density, $B_2(T)$ is the second virial coefficient, $\alpha(T)$ is the contribution of the repulsive forces to the second virial coefficient, $G(\eta)$ is the average pair distribution function at contact for equivalent hard convex bodies, and kT has its usual meaning. They adopted the following form for $G(\eta)$, which was found to be accurate for hard convex bodies [8,9].

$$G(\eta) = \frac{1 - \gamma_1\eta + \gamma_2\eta^2}{(1-\eta)^3} \quad (2)$$

where γ_1 and γ_2 are chosen to reproduce the correct third and fourth virial coefficients of the bodies and η is the packing fraction. In practice γ_1 and γ_2 can be approximated in terms of a single nonsphericity parameter γ, equal to unity for hard spheres. The parameters γ_1 and γ_2 have been defined in terms of γ as [8]

$$\gamma_1 = 3 - \frac{1 + 6\gamma + 3\gamma^2}{1 + 3\gamma} \quad (3)$$

$$\gamma_2 = 3 - \frac{2 + 2.64\gamma + 7\gamma^2}{1 + 3\gamma} \quad (4)$$

The packing fraction, η, is given by

$$\eta = \frac{b\rho}{1 + 3\gamma} \quad (5)$$

where b is the van der Waals covolume or effective molecular volume and can be defined in terms of α as

$$b = \alpha + T\frac{d\alpha}{dT} \quad (6)$$

Once the intermolecular potential is known, the parameters $B_2(T)$, $\alpha(T)$, and $b(T)$ can be found by integrations:

$$B_2(T) = 2\pi N_A \int_0^\infty (1 - e^{-u/kT}) r^2 dr \qquad (7)$$

$$\alpha(T) = 2\pi N_A \int_0^{r_m} (1 - e^{-u_0/kT}) r^2 dr \qquad (8)$$

where N_A is Avogadro's number, and $u_0(r)$ is the repulsive part of $u(r)$.
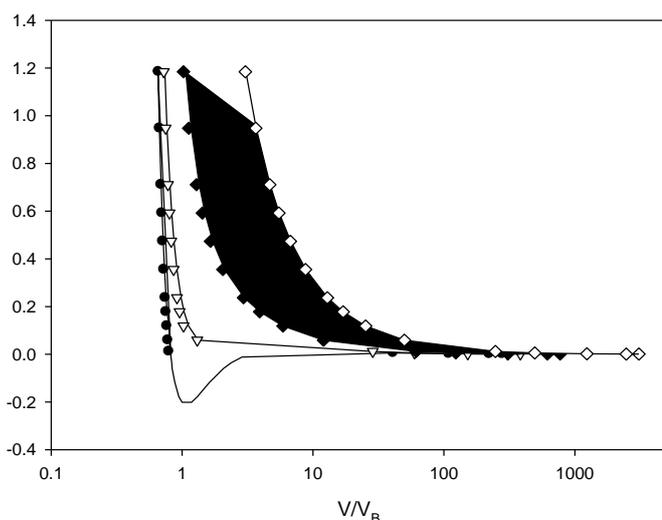
Fig. 1. Reduced *P-V* isotherms at 110 K ($\bullet$), 150 K (∇), 300 K ($\blacklozenge$), and 1200 K ($\lozenge$). The curves (solid lines) represent the equation of state, and the points indicate the experimental data

3. Comparison with experiment

Because of the above mentioned applications of argon we decided to calculate its thermodynamic properties. We used Lennard-Jones (12-6) potential and equations (6-8) for calculation $B_2(T)$, $\alpha(T)$ and $b(T)$. The best value of γ for argon that is a noble gas is equal 1 [8] , $\varepsilon/k=120$ K, that ε is the depth of the potential well and $\sigma=3.405\text{Å}$ that σ is the distance at which the inter particle potential is zero. The *p-v* isotherms are shown in Fig. 1 at four temperatures, two below and two above the critical temperature($T_c=150.66$).
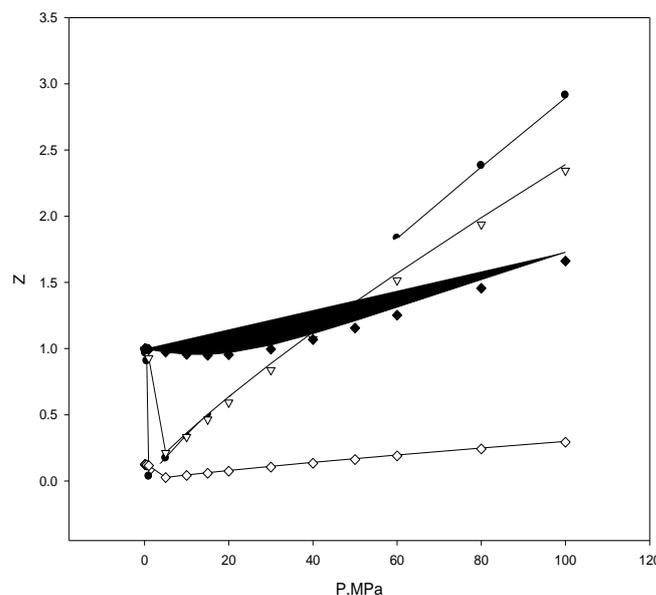
Fig. 2. The plot of compressibility factor, *Z*, as a function of pressure at 110 K ($\bullet$), 150 K (∇), 300 K ($\blacklozenge$), and 1200 K ($\lozenge$). The curves (solid lines) represent the equation of state, and the points are taken from Ref.[10].

3.1. Compressibility Factor

The compressibility factor, defined as $Z=p/\rho kT$, shows the extent of deviation from ideality. Once the equation of state is known, the compressibility factor can be calculated at any temperature and pressure. Compressibility isotherms have been calculated from the equation of state over pressure range of 0.08 to 100 MPa and are compared with the experiment values [10] in Fig. 2. Average absolute deviation (AAD) that defines in Eq. (9) is about 2.5%.

$$(9) \quad AAD = 100/NP \sum_{i=1}^{NP} \left| Z_{i,Cal} - Z_{i,Exp.} \right| / Z_{i,Exp.}$$

where *NP* represents the number of data points examined.

3.2. Fugacity coefficient

The fugacity is related to the equation of state by the formula

$$\ln \frac{f}{P} = \int_0^P (Z-1)\frac{dP}{P} \qquad (10)$$

where f is the fugacity and Z is the compressibility factor. The ratio f/P is called the fugacity coefficient. The fugacity coefficient can be calculated from Eq. (10) in conjunction with the equation of state. Since the analytical calculation of the above integra is not straightforward, we proceeded numerically. The calculated isotherms of the fugacity coefficient over the pressure range of 1 to 226 bar and their good agreement with the calculated values in Ref. 11 are shown in Fig. 3.
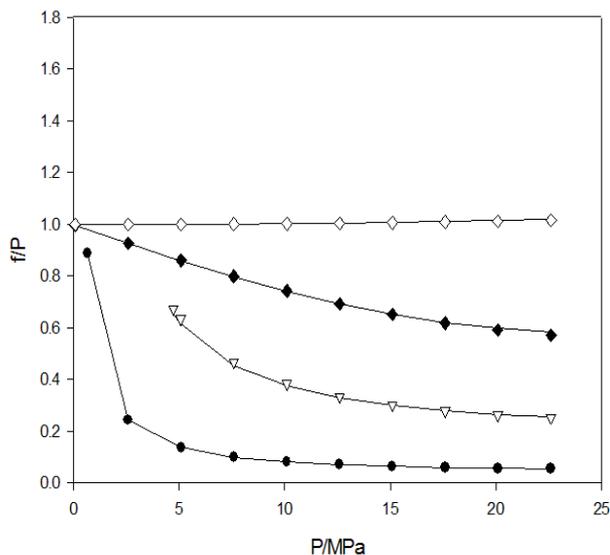
Fig. 3. The plot of fugacity coefficient, f/P, is a function of pressure at 110 K ($\bullet$), 150 K (∇), 200 K ($\blacklozenge$), and 400 K ($\Diamond$). The curves (solid lines) represent the equation of state, and the points are taken from Ref. [11].

4. Conclusion

In the present work we have predicted the thermodynamic properties of argon using a statistical-mechanical equation of state. The present equation of state is accurate and simple in form, needs less input data, and has a statistical-mechanical basis. The temperature-dependent parameters of the equation of state can be calculated from three sets of integrations if the intermolecular pair potential is known.

Our calculated results are in very good agreement with the experimental values in Ref. 10 and 11. Higher deviations at low temperatures can be attributed to the inherent in accuracies in the low temperature second virial coefficients.

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