



Thermodynamic Properties for Argon

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Abstract

An analytical equation of state is 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 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 temperature-dependent parameters. The equation of state has been applied to calculate thermodynamic properties including the internal energy, the enthalpy, the entropy, the heat capacity at constant pressure, and the speed of sound for argon. The theoretical results are in good agreement with the experimental data.

Keywords: Thermodynamic, Argon

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 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 monatomic, 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,

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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,

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

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 and can be defined in terms of α as

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

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

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

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

where N_A is Avogadro's number, and $u_0(r)$ is the repulsive part of $u(r)$.

3. Comparison with Experiment

We used Lennard-Jones (12-6) potential 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], $\epsilon/k=120$ K and $\sigma=3.405\text{\AA}$.

3.1. Internal Energy and Enthalpy

The excess internal energy can be found from

$$U^{ex} = \int_0^\rho \frac{1}{\rho^2} [p - T(\frac{d p}{d T})_v] d\rho \quad (9)$$

this yields

$$\frac{U^{ex}}{NkT} = -\rho T \left\{ \frac{d B_2}{d T} + \frac{(1+3\gamma)}{b} \left[\frac{(b-\alpha) \left[\frac{[2-(1+\gamma_1)\eta - \gamma_2(2-3\eta)]\eta}{2(1-\eta)^2} + \eta + \gamma_2 \ln(1-\eta) \right]}{\gamma_2 \ln(1-\eta)} - \frac{\alpha}{b} \frac{d b}{d T} + \frac{(3-\gamma_1)\eta^2 - (1+\gamma_1)\eta^3 + \gamma_2(2-5\eta+5\eta^2)\eta}{2(1-\eta)^3} \right] \right\} \quad (10)$$

The excess internal energy is the internal energy relative to the ideal gas at the same temperature and pressure. The internal energy can be found by adding the excess internal energy and the internal energy of the ideal gas, which can be calculated via the following equation [11].

$$\frac{U}{NkT} = \frac{3}{2} + \frac{U^{ex}}{NkT} \quad (11)$$

Shown in Fig. 1 are the isobars of internal energy and their comparison with the experimental values in Ref. 10. The average absolute deviation is 5%.

The enthalpy can be found by the equation, $H = U + PV$.

Shown in Fig. 2 are the isobars of enthalpy and their comparison with the experimental values in Ref. 10. The average absolute deviation is 4%.

3.4. Entropy

The excess entropy is the entropy relative to the entropy of the ideal gas at the same

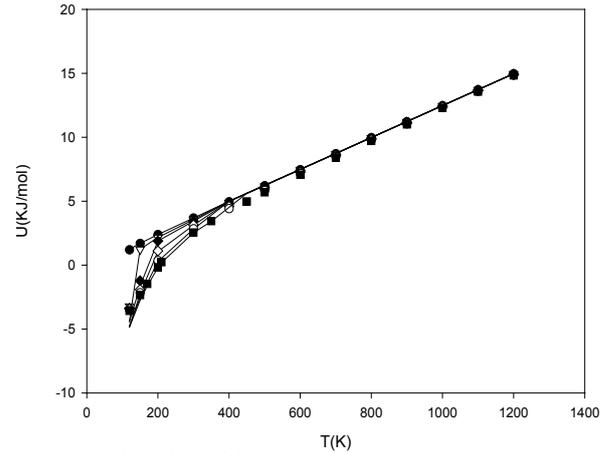


Fig. 1. The plot of internal energy, U , as a function of temperature at 1 bar (\bullet), 30 bar (∇), 50 bar (\blacklozenge), 100 bar (\diamond), 150 bar (\circ), and 200 bar (\blacksquare). The curves (solid lines) represent the equation of state, and the points are taken from Ref. 10.

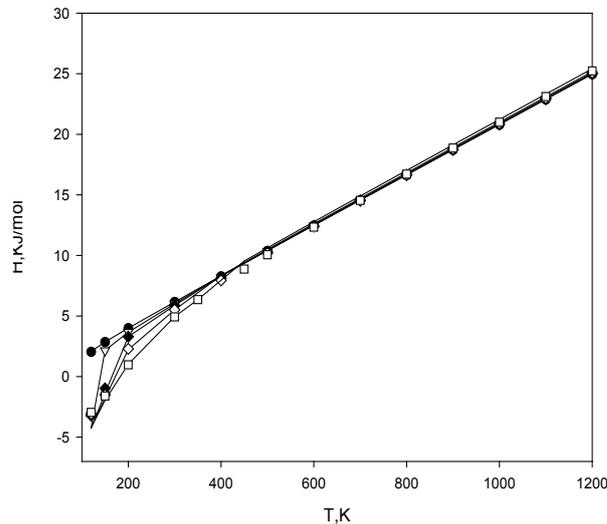


Fig. 2. The plot of enthalpy, H , as a function of temperature at 1 bar (\bullet), 30 bar (∇), 50 bar (\blacklozenge), 100 bar (\diamond), and 200 bar (\square). The curves (solid lines) represent the equation of state, and the points are taken from Ref. 10.

temperature and pressure and is defined as

$$\frac{S^{ex}}{Nk} = \int \frac{1}{\rho^2} \left[\left(\frac{d p}{d T} - \rho \right) \right] d\rho \quad (12)$$

where S^{ex} is the excess entropy. For the present equation of state, this yields

$$\frac{S^{ex}}{Nk} = (b - B_2 - T \frac{d B_2}{d T}) \rho + (1 + 3\gamma) \times \left\{ \left[\gamma_2 \ln(1-\eta) - \frac{(3\gamma_2 - \gamma_1 - 1)\eta^2 + 2(1-\gamma_2)\eta}{2(1-\eta)^2} \right] - \frac{\alpha}{b^2} T \frac{d b}{d T} \right\} \left[\gamma_2 \ln(1-\eta) + \frac{(5\gamma_2 - \gamma_1 - 1)\eta^3 + (3-\gamma_1 - 5\gamma_2)\eta^2 + 2\gamma_2\eta}{2(1-\eta)^3} \right] \quad (13)$$

The entropy S can be calculated by adding the excess entropy to the entropy of the ideal gas [12] at the same temperature and pressure via the following equation.

$$\frac{S}{Nk} = \frac{S^{ex}}{Nk} + \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{e^{5/2}}{\rho N} \right] \quad (14)$$

where m is the molecular weight.

The isobars of S have been calculated with Eqs. (1), (13), and (14), and they are compared with experimental data in Ref. 10 in Fig. 3. The average absolute deviation is 2.4%.

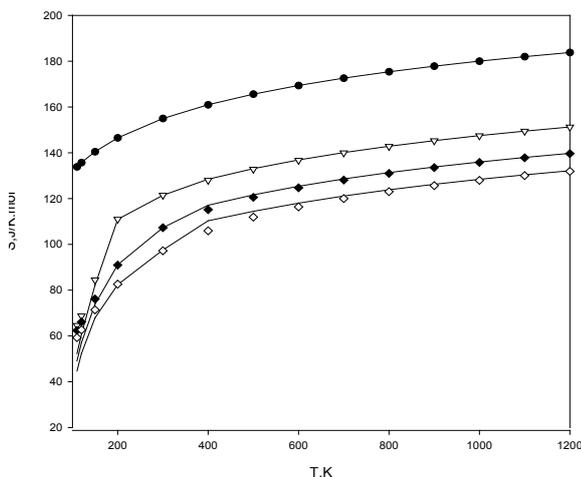


Fig. 3. The plot of entropy, S , as a function of temperature at 1 bar (●), 50 bar (□), 200 bar (◆), 500 bar (◇). The curves (solid lines) represent the equation of state, and the points are taken from Ref. 10.

3.5. Heat Capacities

The heat capacity at constant volume is defined as

$$C_V = T \left(\frac{dS}{dT} \right)_V \quad (15)$$

For the present equation of state C_V is

$$C_V = \left(T \frac{db}{dT} - 2T \frac{dB_2}{dT} - T^2 \frac{d^2B_2}{dT^2} \right) \rho - \frac{(1+3\gamma)}{b} \left(T \frac{db}{dT} [\gamma_2 \ln(1-\eta)] + \frac{(7\gamma_2 - \gamma_1 - 1)\eta^3 + (3-3\gamma_1 - 5\gamma_2)\eta^2 + 2(\gamma_2 + 1)\eta}{2(1-\eta)^3} \right) + \frac{\alpha}{b^2} \left(T \frac{db}{dT} \right)^2 \times \left[\frac{(6\gamma_2 - \gamma_1 - 1)\eta^4 + 2(2-\gamma_1 - 4\gamma_2)\eta^3 + 7\gamma_2\eta^2 - 2\gamma_2\eta}{(1-\eta)^4} - 2\gamma_2 \ln(1-\eta) \right] + \frac{\alpha}{b} T^2 \frac{d^2b}{dT^2} \times \left[\gamma_2 \ln(1-\eta) + \frac{(5\gamma_2 - \gamma_1 - 1)\eta^3 + (3-\gamma_1 - 5\gamma_2)\eta^2 + 2\gamma_2\eta}{2(1-\eta)^3} \right] + \quad (16)$$

The heat capacity at constant pressure can be obtained through the thermodynamic relation,

$$C_P = C_V + \frac{T\alpha_T^2}{\beta\rho} \quad (17)$$

where α_T is the thermal expansion and β is the isothermal compressibility. The parameter α_T and β are defined as

$$\alpha_T = \frac{-1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P \quad \text{and} \quad \beta = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T \quad (18)$$

The following formulas have been obtained from the equation of state for the parameter α_T and β .

$$\alpha_T = \rho^3 RT \left\{ \frac{dB_2}{dT} + \frac{d\alpha}{dT} [G(\eta) - 1] + \frac{P}{\rho^2 k T^2} + \frac{\alpha db}{b dT} \left[\frac{3\eta G(\eta)}{1-\eta} + \frac{2\gamma_2\eta^2 - \gamma_1\eta}{(1-\eta)^3} \right] \right\} / \left\{ 2p + \rho k T \left[-1 + \alpha \rho \left[\frac{3\eta G(\eta)}{1-\eta} + \frac{2\gamma_2\eta^2 - \gamma_1\eta}{(1-\eta)^3} \right] \right] \right\} \quad (19)$$

and

$$\beta = 2p + \rho k T \left[-1 + \alpha \rho \left[\frac{3\eta G(\eta)}{1-\eta} + \frac{2\gamma_2\eta^2 - \gamma_1\eta}{(1-\eta)^3} \right] \right] \quad (20)$$

The heat capacities can be calculated from Eqs. (1), (16), (17), (18), (19) and (20). The calculated isobars of heat capacity at constant pressure are shown in Fig. 5, and are compared with the experimental values in Ref. 10.

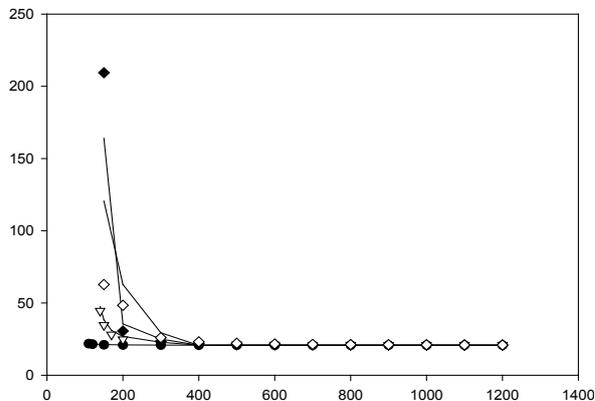


Fig. 4. The plot of heat capacity at constant pressure, C_P , as a function of temperature at 1 bar (●), 30 bar (▽), 50 bar (◆), 100 bar (◇). The curves (solid lines) represent the equation of state, and the points are taken from Ref. 10.

3.6. Speed of Sound

The speed of sound can be calculated from the equation

$$W = \left[\frac{C_p}{C_v} \frac{1}{M} \left(\frac{\partial p}{\partial \rho} \right)_T \right]^{1/2} \quad (21)$$

where W is the speed of sound and M is the molar mass. Equations (1) and (21) together with the experimental values of C_p/C_v have been used to calculate the speed of sound in argon. The calculated isobars of the speed of sound are shown in Fig. 5 and compared with the experimental data in Ref. 10. For the higher-pressure isobars, the maximum deviations extend to $\pm 8\%$.

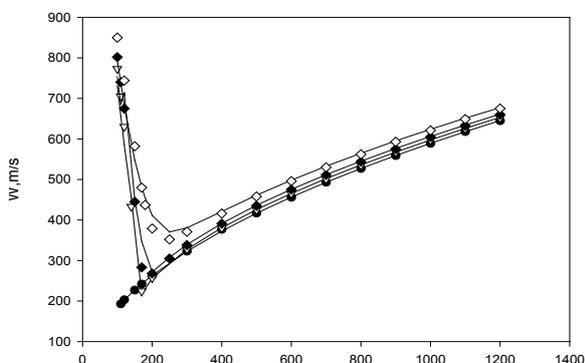


Fig. 5. The plot of speed of sound, W , as a function of temperature at 1 bar (\bullet), 50 bar (∇), 100 bar (\blacklozenge), 200 bar (\diamond). The curves (solid lines) represent the equation of state, and the points are taken from Ref. 10.

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 on the internal energy, enthalpy, entropy and speed of sound 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 inaccuracies in the low temperature second virial coefficients. The heat capacity involves a second differentiation of the temperature-dependent parameters of the equation of state, and consequently, the errors become order of magnitude exaggerated.

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