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Note

An Analytical Equation of State for Mercury

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This paper presents a procedure for predicting the equation of state of mercury, by including mercury in the scope of a new statistical mechanical equation of state that is known for normal fluids. The scaling constants are the latent heat of vaporization and the density at the melting temperature, which are related to the cohesive energy density. Since experimental data for the second virial coefficient of mercury are scarce, a corresponding-states correlation of normal fluids is used to calculate the $B(T)$ of mercury. The free parameter of the ISM equation, λ, compensates for the uncertainties in $B(T)$. Also, we can predict the values of two temperature-dependent parameters, $\alpha(T)$ and $b(T)$, with satisfactory accuracy from a knowledge of ΔH_{vap} and ρ_{m}, without knowing any details of the intermolecular potentials. While the values of $B(T)$ are scarce for mercury and the vapor pressure of this metal at low temperatures is very small, an equation of state for mercury from two scaling parameters (ΔH_{vap}, ρ_{m}) predicts the density of Hg from the melting point up to 100° above the boiling temperature to within 5%.

KEY WORDS: cohesive energy; corresponding states; equation of state; mercury.

1. INTRODUCTION

Because of the widespread use of mercury in modern industry, knowledge of its physical properties is necessary. Accurate knowledge of the density of mercury is essential, because of its use as a pressure exerting medium. In fact there is a large amount of experimental work on the density and the other thermodynamic parameters of mercury in the literature.

The density of mercury at atmospheric pressure has been measured by Cook and Stone [1]. Bridgman [2] and Hayward [3] determined the

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volume change of mercury with pressure. Davis and Gordon [4] determined the value of the density of mercury by measurements of the velocity of sound as a function of temperature and pressure. Holman and ten Seldam [5] corrected the measured values of Davis and Gordon by comparing their isothermal secant bulk modulus at a certain temperature and pressure with the highly accurate secant bulk modulus measured by Hayward. The heat capacity of mercury from 15 to 330 K has been measured by Busey and Giauque [6]. They also determined the heat of fusion at the melting point and combined the results with calorimetric and vapor pressure data at higher temperatures, and the Sackur–Tetrode equation, to determine the thermodynamic properties of solid, liquid, and gaseous mercury. The vapor pressure of mercury has been measured by a number of observers, but of these, the data of Smith and Menzies [7] and Beattie et al. [8] have been recommended.

Metals in the liquid state can be treated as simple monatomic systems, and like the normal fluids, they are examples of systems to which the (group) law of corresponding states [9], equation of state [10], and law of rectilinear density [11, 12] are applied. Theoretical equilibrium thermodynamic properties of mercury have not been well investigated. However, Holman and ten Seldam [5] calculated the density of mercury in the temperature range 293–323 K and the pressure range 0–300 MPa. They applied a double polynomial equation for the density of mercury to calculate the thermodynamic properties and evaluated the isobaric secant and tangent volume thermal expansion coefficients and isothermal secant and tangent compressibilities as a function of temperature and pressure.

Values of the second virial coefficient, which is the main parameter in studying equilibrium thermodynamic properties, are not available over a wide range of temperatures for mercury. Douglas et al. [13] have, in effect, assumed a second virial coefficient, based on a three-constant equation derived from rather uncertain stability data for diatomic mercury gas, and combined the various results to obtain the best overall fit for the heat of dissociation of Hg_2 and the entropy of the liquid.

In the circumstances where experimental data for the second virial coefficient are scarce and theoretical calculations are not in reasonable agreement with experimental data, the existence of an equation of state for predicting the thermophysical properties at desire temperatures and pressures is necessary. With the recent advances in statistical–mechanical theories, we are able to predict the physical properties of compressed normal liquids [14], their mixtures [15], and molten alkali metals [16]. We hope that this method is applicable to mercury, too.

This paper presents a procedure for predicting the equation of state for mercury from properties that are readily available at ordinary pressure and temperature. Here we use the heat of vaporization and the liquid density at the melting point as scaling parameters that can correlate and predict the thermophysical behavior of mercury at a moderate range of temperatures and saturation pressures.

2. THEORY

In this method, we use the theoretical equation of state of Ihm, Song, and Mason (ISM) [17], which is based on the statistical-mechanical perturbation theory for the condensed fluids:

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

In Eq. (1), P is the pressure, ρ is the number (molar) density, kT has its usual meaning, B is the second virial coefficient, α is a temperature-dependent parameter that scales for the softness of the repulsive forces, and b is a temperature-dependent analogue of the van der Waals covolume. The parameters B, α, and b are related to the intermolecular potentials and can be calculated by integrations, and λ is a constant. We can write the corresponding-states results in the form

$$G(b\rho)^{-1} = \alpha\rho\left[Z - 1 + \frac{(\alpha - B)\rho}{1+0.22\lambda b\rho}\right]^{-1} = 1 - \lambda b\rho \tag{2}$$

where $Z = P/\rho RT$ is the compressibility factor and $G(b\rho)$ is an average pair distribution function at contact for equivalent hard convex bodies. Here $G(b\rho)^{-1}$ is a function of $b\rho$, i.e., it varies linearly with $b\rho$ with the slope of λ. From the P–V–T data together with the value of α, b, and B, λ can be calculated by iteration. We utilize Eq. (1) as the equation of state for mercury and consider the cohesive energy density and the density at the melting point as the only input data. The parameter ΔH_{vap} is determined from the experimental vapor pressure data using the Clausius–Clapeyron equation.

3. CORRELATION PROCEDURE

The second virial coefficient $B(T)$ has a control role in the application of Eq. (1): it is used both directly and as the source of a scaling constant for the calculation of $\alpha(T)$ and $b(T)$.

For mercury, neither accurate potential functions nor experimental values of $B(T)$ over a whole range of temperatures are known. Instead we propose that the $B(T)$ values be calculated from a corresponding-states correlation used for normal fluids [14, 15]. We do not need to be concerned with the uncertainties in $B(T)$, because the adjustable parameter of the equation of state, λ, compensates for the associated uncertainties [18]. As mentioned earlier, the two scaling parameters in the correlation are ΔH_{vap} and ρ_{m}.

The corresponding-states correlation for $B(T)$ can be presented by the empirical expression

$$B\rho_{\mathrm{m}} = 0.403891 - 0.076484(\Delta H_{\mathrm{vap}}/RT)^2 - 0.0002504(\Delta H_{\mathrm{vap}}/RT)^4 \qquad (3)$$

Once $B(T)$ is known, the parameters $\alpha(T)$ and $b(T)$ follow from almost any reasonable two-constant effective pair potential; the results can also be scaled by ρ_{m} and $\Delta H_{\mathrm{vap}}/R$ values, and are fitted by the expressions

$$\alpha\rho_{\mathrm{m}} = a_1 \exp[-c_1(RT/\Delta H_{\mathrm{vap}})] + a_2\{1 - \exp[-c_2(\Delta H_{\mathrm{vap}}/RT)^{1/4}]\} \qquad (4)$$

$$\begin{aligned} b\rho_{\mathrm{m}} = {} & a_1[1 - c_1(RT/\Delta H_{\mathrm{vap}})] \exp[-c_1(RT/\Delta H_{\mathrm{vap}})] \\ & + a_2\{1 - [1 + 1/4c_2(\Delta H_{\mathrm{vap}}/RT)^{1/4}] \exp[-c_2(\Delta H_{\mathrm{vap}}/RT)^{1/4}]\} \end{aligned} \qquad (5)$$

where

$$a_1 = -0.1053, \qquad a_2 = 2.9359$$

$$c_1 = 5.7862, \qquad c_2 = 0.7966$$

This expressions are based on the results obtained with a Lennard–Jones (6–12) potential [19].

We used the tabulation of Vargaftik [20] for calculation of the liquid densities and obtained the values of ΔH_{vap} directly using various vapor pressure data. The characteristic free parameter of the mercury in the equation of state, λ, can be calculated from the two scaling constants (ΔH_{vap}, ρ_{m}) by iteration because this parameter is just a correction factor.

4. RESULTS AND DISCUSSION

The present work shows how the equation of state of a compressed liquid gives a statistical–mechanical basis for liquid metals [16]. It extends the ISM equation of state to include mercury, which is a supplement to the previous work [16]. It should be noted that since the second virial coefficient, $B(T)$, of mercury is not known experimentally, the present method can be used for mercury with reasonable accuracy only by knowing two parameters, ΔH_{vap} and ρ_{m}. Although the uncertainties associated with extrapolation cannot be ruled out, the corresponding-states correlation for calculation of the second virial coefficient is of great importance, since the extrapolation to the metallic region yields parameters of the analytical equation of state. We used Eqs. (3)–(5) to calculate the parameters of equation of state.

The results show that two vapor-pressure data points, to calculate the heat of vaporization and the density at the melting point, are sufficient to estimate the thermodynamic properties from melting temperature up to 100° above the boiling temperature for mercury. The calculated value of $\Delta H_{vap}/R$ is 7223.3607 K.

Using P–T data [20], we have calculated the density of mercury from −38.83 to 450°C, which is a much wider range than that of the Holman and ten Seldam [5] calculations. The results are shown in Table I. In metals, although the interatomic potentials are inherently different in the liquid and vapor states, Eq. (1) with the Lennard–Jones (12–6) potential used to calculate $\alpha(T)$ and $b(T)$ still produces results within a reasonable accuracy (5%). The reason is that α and b depend only on the intermolecular repulsive forces and are therefore relatively insensitive to the details of the shape of the intermolecular potential.

The average contact pair distribution function can be calculated with a knowledge of ΔH_{vap} and ρ_m, by which the linear dependence of G^{-1} vs $b\rho$ is given a strong basis in statistical mechanics [14]. The calculated value of λ for mercury is 0.449. It is a free parameter that incorporates the inaccuracy associated with the temperature-dependent constants.

The present work also shows to what extent the density of mercury can be extended, namely, from the melting point up to 100° above the

Table I. The Physical Properties of Mercury

T (°C)	P (bar)	ρ_{expt} (mol · L^{-1})	ρ_{calc} (mol · L^{-1})	Dev. (%)
−38.83	3.066×10^{-9}	68.25	68.25	0.00
0.00	2.728×10^{-7}	67.77	68.89	1.65
50.00	1.786×10^{-5}	67.16	69.31	3.20
100.00	3.745×10^{-4}	66.55	69.29	4.11
150.00	3.778×10^{-3}	65.96	68.86	4.39
200.00	2.315×10^{-2}	65.36	68.11	4.20
250.00	9.959×10^{-2}	64.77	66.93	3.33
300.00	0.3301	64.17	65.47	2.02
350.00	0.8989	63.57	63.71	0.22
400.00	2.1024	62.97	61.68	−2.04
450.00	4.362	62.36	59.48	−4.61

boiling temperature and the results are within 5%. There is a systematic variation of deviations between +4% at 100°C and −4.6% at 450°C, with 0% at boiling point. The results of this work do not allow us to account for this observation.

In summary, the present work indicates that the physical properties can be predicted from just two scaling constants, the heat of vaporization and the liquid density at melting temperature, which are readily measurable. Determination of the equation of state for mercury from the heat of vaporization with respect to the second virial coefficients, which are experimentally scarce, gives excellent results that are within 5%.

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