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Equation of State for Mercury

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Abstract

An analytical equation of state by Song and Mason is developed to calculate the PVT properties of mercury. The equation of state is based on the statistical-mechanical perturbation theory of hard convex bodies and can be written as a fifth-order polynomial in the density. There exists three temperature-dependent parameters in the equation of state; the second virial coefficient, an effective molecular volume, and a scaling factor for the average contact pair distribution function of hard convex bodies. The temperature-dependant parameters have been calculated using corresponding-states correlations based on the heat of vaporization and the liquid density at the melting point. The average absolute deviation for the calculated density of mercury in the saturation and compressed state is 0.38 .

Keywords: Equation of State, Heat of Vaporization, Thermodynamic Properties.

Introduction

One of the heaviest transition metals, known as quicksilver, with many unique properties and applications, is mercury. This metal has been used in many household, medical, and industrial products. A few examples are its applications in fluorescent and high intensity discharge lamps, old alkaline batteries and some button batteries, fungicides for seeds and turf, thermometers, dental amalgam, chemistry sets, older toys and games, thermostats, electrical switches, catalysts in industrial plants, and its ability to form organic species that are particularly stable in organic liquids [1].

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 and theoretical works on the density and thermodynamic parameters of mercury in the literature [2-9]. A critical review on the thermophysical properties of mercury is given by Holmen and ten Seldam [10]. Due to the difficulties in obtaining experimental data, especially at high temperatures and high pressures, there is a large demand on theoretical methods to predict the P-V-T properties and other thermodynamic properties of mercury.

Recently molecular simulation methods [11,12] have been applied to calculate the equilibrium and transport properties of mercury. Although very accurate in nature, molecular simulation methods are computationally expensive and need accurate potential energy functions for this purpose. For example, in the previous works by Raabe et al. [12,13] on the molecular dynamic simulation of mercury they showed that even very accurate ab initio potential energy functions [14,15] can't well reproduce the properties of liquid mercury, therefore they added a term due to the many-body

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interactions to correct for it.

Prediction of the properties of the liquid phase using correlation schemes is another method, which is widely used in the case of pure fluids and fluid mixtures. Recently Eslami [8,9] has developed corresponding states correlations to predict the liquid density of metals, including mercury, in the saturation and compressed states. These methods, however, can predict the liquid density but do not show the gas-liquid continuity. Equations of states are other well-known methods for the prediction of the thermodynamic properties. Mehdipour and Boushehri [16] have applied a statistical-mechanical equation of state [17] to calculate the PVT properties of mercury at saturation states. Their calculations are restricted to the saturation states, and obviously low to moderate pressures. It is the purpose of this paper to develop a statistical-mechanical equation of state by Song and Mason [18] to mercury over a wide range of temperatures and pressures. It is predicted the equation of state for mercury from heat of vaporization and the liquid density at the melting point as scaling parameters which, as we will show it can correlate and predict the thermophysical behavior of mercury over a wide range of temperatures and pressures.

Theoretical Equation of State

Song and Mason [18] proposed an analytical equation of state for convex-molecular fluids based on statistical-mechanical perturbation theory. The equation of state is:

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

where P is the pressure, ρ is the molar (number) density, $B_2(T)$ is the second virial coefficient, α(T) is the contribution of the repulsive forces to the second virial coefficient, G(η) is the average pair distribution function at contact for equivalent hard convex bodies, ηis the packing fraction, and kT is the thermal energy per one molecule. Song and Mason [18] adopted the following form for G(η), which is shown to be accurate for hard convex bodies [18,19].

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

In equation 2, γ_1 and γ_2 are chosen to reproduce the correct third and fourth virial coefficients. 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 [18]

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

and

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

the packing fraction, η, is given by

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

where b is the van der Waals co-volume and can be defined in terms of α as [18]:

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

Once the intermolecular potential energy function is known, the temperature-dependent parameters $B_2(T)$, α(T), and b(T) can be found by three integrations, and γ is the best found by fitting available P-V-T data [18].

The second virial coefficient $B_2(T)$ has a central role in the equation of state, Eq. (1); it is used both directly and as the source of a scaling constant for calculation of α(T) and b(T) [18]. In fact $B_2(T)$ is used to determine the Boyle parameters, the Boyle volume and temperature, and it is shown that when reduced in terms of the Boyle volume α(T) and b(T) are universal functions of the reduced temperature [20]. This means that one can also use experimental values of $B_2(T)$ over a wide range of temperatures to determine the Boyle parameters, and hence α(T) and b(T), but accurate potential energy function for the calculation of $B_2(T)$ are scarce. Although some nearly accurate ab initio pair potentials, are reported in the literature for mercury, Raabe et. al. [12] in their extensive molecular dynamics calculation have shown that even these

potentials can not be used to calculate PVT properties for high-density vapor and liquid mercury. They showed that due to strong many-body interactions in mercury, it is essential to add an additional term to incorporate these interactions. In these circumstances, fortunately, there are some corresponding-states methods by which the second virial coefficients and the other two temperature-dependent parameters can be calculated with reasonable accuracy [21-25].

In these methods we need two scaling constants, one to reduce the second virial coefficient and one to reduce the temperature. In the conventional law of corresponding-states the critical temperature and the critical volume are used for this purpose, but the critical parameters of metals are either scarce or not measured accurately due to the experimental difficulties at the critical point. Recently [21] it is shown that using the liquid density at an specified point like the normal boiling point and the surface tension or the heat of vaporization, as energy parameters, to reduce the temperature, one can generate universal plots of the reduced second virial coefficient versus the reduced temperature.

Boushehri and Mason [24] chose the heat of vaporization divided by R as the temperature parameter to reduce the temperature and the liquid density at the triple point to reduce the second virial coefficients. They proposed the following correlation for the prediction of the second virial coefficients:

$$B_2(T)\rho_m = 0.403891 - 0.076484(\Delta H_{vap}/RT)^2 - 0.0002504(\Delta H_{vap}/RT)^4 \quad (7)$$

Song and Mason [20] showed that the reduced temperature-dependant parameters, $\alpha(T)$ and $b(T)$, are universal functions of the reduced temperature when reduced in terms of the Boyle parameters. Also they showed that $\alpha(T)$ and $b(T)$ are relatively insensitive to the detail of the potential energy function [20]. Therefore, they proposed two empirical formulas for reduced α (T) and b(T) in terms of the reduced temperature.

We employed the same empirical formulas proposed by Song and Mason [23] and rescaled the coefficients of the formulas to consider the effect of changing the scaling constants from the Boyle parameters to heat of vaporization and the liquid density at the melting point, i.e

$$\alpha(t)\rho_m = \alpha_1 \exp[-c_1(RT/\Delta H_{vap})] + \alpha_2\{1-\exp[-c_2(\Delta H_{vap}/RT)^{1/4}]\} \quad (8)$$

$$b(T)\rho_m = a_1[1-c_1(RT/\Delta H_{vap})]\exp[-c_1(RT/\Delta H_{vap})] + a_2\{1-[1+\frac{1}{4}c_2(\Delta H_{vap}/RT)^{1/4}]\exp[-c_2(\Delta H_{vap}/RT)^{1/4}]\} \quad (9)$$

where a_1=-3.688, a_2=0.4126
c_1=4.1163, c_2=1.7518

In this work we apply the equation of state, Eq. 1, with the temperature-dependent parameters determined using the corresponding-states correlation based on heat of vaporization and the liquid density at the melting point as scaling constants, Eqs. 7-9, to determine PVT properties of mercury over a wide range of temperatures and pressures.

Results

We have employed Eq. 1, together with correlation equations, Eqs. 7-9, to calculate the saturated and compressed liquid density of mercury over a wide range of temperatures and pressures.

The values of input parameters for calculating the temperature-dependant parameter, $\alpha(T)$ and $b(T)$, are reported in Table 1. Putting the value of γ=1 as for spherical particles, it gives the liquid density of mercury. The saturation liquid densities are reported in Table 2, and are compared with experimental data and with the predictions from literature [16]. The calculated results for gas densities and comparison with experimental data [16] are reported in Table 3. The method has also calculated the compressed liquid density of mercury over a wide range of pressures. The results are compared with experimental data [10] in Table 4.

Conclusion

Comparison of our calculated densities in Table 2, 3 and 4 with experiment [10, 26] show that the present equation of state can well reproduce the density of mercury over a wide range of temperatures and pressures.

There is no need to know accurate potential energy function, or to know the values of the critical constants for the calculation of the second virial coefficients. The temperature-dependant parameters can be calculated using simple scaling constants, which are readily available.

Our results in Table 2 show that the present equation of state predict PVT properties of mercury over a wider range of temperatures and pressures and is more accurate than the previous equation of state [16].

Although the empirical formulas for α and b, Eqs. 8, 9, are originally presented by Song and Mason [23] based on fitting the results for a Lennard-Jones potential, these equations still predict good results for PVT properties of mercury, for which the Lennard-Jones potential is not valid. This is because of the fact that the temperature dependant parameters, α(T) and b(T), are insensitive to the details of the potential energy functions and are just obtainable from the repulsive branch of the potential, or as it is described in this work by knowing just to readily available scaling constants.

Table 1. The values of input parameters for mercury

ΔH_{vap} [J.mol^{-1}]	ρ_m [mol.L^{-1}]	. γ
60055.02	68.25	1.0

Table 2. The calculated results for the saturated liquid density of mercury compared with experiment [26] and with the predictions from our previous equation of state [16].

				Dev(%)	
T(K)	P(bar)	ρ_{exp}(mol.m^{-3})	$\rho_{cal.}$(mol.m^{-3})	This work	Ref. 16
273.15	2.73×10^{-7}	67768.46	67971.83	0.30	1.65
323.15	1.79×10^{-5}	67157.72	67344.15	0.28	3.2
373.15	3.75×10^{-4}	66554.11	66673.27	0.18	4.11
423.15	3.78×10^{-3}	65955.69	65997.45	0.06	4.39
473.15	2.32×10^{-2}	65360.5	65339.33	-0.03	4.2
523.15	9.96×10^{-2}	64766.56	64709.7	-0.09	3.33
573.15	3.30×10^{-1}	64171.78	64110.45	-0.1	2.02
623.15	8.99×10^{-1}	63574.1	63537.39	-0.06	0.22
673.15	2.10	62970.94	62980.34	0.01	-2.04
723.15	4.36	62360.3	62425.25	0.10	-4.61
773.15	8.22	61741.69	61853.51	0.18	
823.15	14.3	61108.62	61241.03	0.22	
873.15	23.5	60465.58	60557.15	0.15	
923.15	36.4	59807.59	59761.1	-0.08	
973.15	54.0	59134.64	58795.84	-0.57	
1023.15	77.2	58446.74	57575.69	-1.49	
1073.15	107	57743.88	55956.79	-3.10	

Table 3. The calculated results for the gas density of mercury compared with experiment [26].

T(K)	P(bar)	ρ_{exp}(mol.m^{-3})	$\rho_{cal.}$(mol.m^{-3})	Dev(%)
273.15	2.73×10^{-7}	1.201×10^{-5}	1.285×10^{-5}	6.98
323.15	1.79×10^{-5}	6.628×10^{-3}	6.647×10^{-4}	0.27
373.15	3.75×10^{-4}	1.206×10^{-2}	1.207×10^{-3}	0.07
423.15	3.78×10^{-3}	1.072×10^{-1}	1.074×10^{-1}	0.21
473.15	2.32×10^{-2}	5.887×10^{-1}	5.886×10^{-1}	-0.01
523.15	9.96×10^{-2}	2.291	2.291	0.02
573.15	3.30×10^{-1}	6.935	6.941	0.08
623.15	8.99×10^{-1}	17.392	17.415	0.14
673.15	2.10	37.743	37.811	0.18
723.15	4.36	73.127	73.316	0.26
773.15	8.22	129.605	129.910	0.24
823.15	14.3	213.648	214.214	0.26
873.15	23.5	332.336	332.888	0.17
923.15	36.4	492.548	492.890	0.07
973.15	54.0	701.610	700.466	-0.16
1023.15	77.2	966.253	962.006	-0.44
1073.15	107	1293.405	1282.907	-0.81

Table 4. The calculated results for the compressed liquid density of mercury compared with experiment [26].

T(K)	P(bar)	ρ_{exp}(mol.m^{-3})	$\rho_{cal.}$(mol.m^{-3})	Dev(%)
293.15	0	67523.254	67808.353	0.42
293.15	500	67657.146	67826.279	0.25
293.15	1000	67789.043	67843.944	0.08
293.15	1500	67918.997	67861.528	-0.08
293.15	2000	68047.007	67879.036	-0.25
293.15	2500	68173.122	67896.278	-0.41
293.15	3000	68297.443	67913.868	-0.56
298.15	0	67462.190	67745.643	0.42
298.15	500	67596.680	67764.470	0.25
298.15	1000	67729.226	67783.592	0.08
298.15	1500	67859.778	67802.354	-0.08
298.15	2000	67988.385	67821.031	-0.25
298.15	2500	68115.099	67839.432	-0.40
298.15	3000	68239.918	67858.179	-0.56
303.15	0	67401.176	67682.163	0.42
303.15	500	67536.314	67702.579	0.25
303.15	1000	67669.458	67723.670	0.08
303.15	1500	67800.608	67742.661	-0.08
303.15	2000	67929.814	67762.560	-0.25
303.15	2500	68057.126	67782.177	-0.40
303.15	3000	68182.493	67802.126	-0.56
308.15	0	67340.212	67618.261	0.41
308.15	500	67475.998	67639.851	0.24
308.15	1000	67609.790	67661.235	0.08
308.15	1500	67741.588	67682.511	-0.09
308.15	2000	67871.342	67703.685	-0.25
308.15	2500	67999.202	67724.572	-0.40
308.15	3000	68125.118	67745.770	-0.56
313.15	0	67279.298	67553.695	0.41
313.15	500	67415.782	67576.613	0.24
313.15	1000	67550.172	67599.345	0.07
313.15	1500	67682.568	67621.961	-0.09
313.15	2000	67812.970	67644.463	-0.25
313.15	2500	67941.379	67666.678	-0.40
313.15	3000	68067.843	67689.173	-0.56
318.15	0	67218.484	67488.612	0.40
318.15	500	67355.615	67512.919	0.23
318.15	1000	67490.653	67537.056	0.07
318.15	1500	67623.648	67561.066	-0.09
318.15	2000	67754.599	67584.952	-0.25
318.15	2500	67883.605	67607.551	-0.41
318.15	3000	68010.6177	67632.392	-0.56
323.15	0	67157.7688	67423.062	0.39
323.15	500	67295.499	67448.819	0.23
323.15	1000	67431.185	67474.419	0.06
323.15	1500	67564.778	67499.879	-0.10
323.15	2000	67696.326	67525.204	-0.25
323.15	2500	67825.881	67550.245	-0.40
323.15	3000	67953.492	67575.483	-0.56

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