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An Analytical Equation of State for Some Saturated Liquid Metals

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An analytical equation of state (EoS) is developed for some saturated molten metals. The equation is that of Ihm, Song and Mason in which the three temperature-dependent parameters, second virial coefficient, van der Waals co-volume, and a scaling parameter, are calculated by means of corresponding states correlations. The required characteristic constants are the heat of vaporization and the density at the melting point, ΔH_{vap} and ρ_{m}, respectively. The EoS is applied to these liquid metals to calculate the density at temperatures higher than their melting points. The results are fairly consistent with experiment, maximum difference less than ±4%.

KEY WORDS: correlation; equation of state; heat of vaporization; liquid metals.

1. INTRODUCTION

Liquid metals exhibit various characteristics that are invaluable in industrial applications. Features such as high boiling temperatures, extended liquid range, high thermal conductivity, low vapor pressure, and high heats of vaporization are very important in machine design and processing operations. Therefore a precise knowledge of their thermodynamic properties seems to be extremely helpful. Unfortunately, for metals, difficult experimental conditions such as high temperatures and low vapor pressures limit the experimental measurements. This has led many investigators to apply various accurate predictive methods. In this respect, modern

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statistical mechanical theories provide powerful tools for thermophysical studies.

In general, thermodynamic and physical properties of fluids can be estimated directly through an equation of state (EOS), which is able to describe the pressure–volume–temperature (*PVT*) behavior of matter on a fundamental theoretical basis. Below, we present an analytical EOS that accurately reproduces the *PVT* dependence of a number of metals over a relatively wide range of temperatures and pressures.

We start with the ISM EOS, which was proposed primarily by Song and Mason [1] and extended later by Ihm et al. [2]. This EOS includes three parameters in the final form, B_2 (T), the second virial coefficient, b (T), the effective van der Waals co-volume, and α (T), a scaling factor. All of these parameters can be calculated by integration, if the intermolecular potential is accurately known. In the absence of such information, the second virial coefficient data suffice to predict the entire (*PVT*) surface of fluids.

For the metals, which are of interest in this work, neither exact intermolecular potential energies nor experimental second virial coefficients exist in the literature. At this point, the most useful method is to predict the second virial coefficient, B_2, and consequently the two other parameters, b and α with the help of the hypothesis of corresponding states which is a useful guide for estimating the behavior of dense gases and liquids. This principle is based on the reduction of the variables using molecular (or atomic) constants (energy and size).

Many investigators have designated methods for predicting the second virial coefficients, and hence the EOS, from different scaling factors such as critical constants [3], the heat of vaporization and liquid density at the triple point [4] and boiling point [5], surface tension and the liquid density at the freezing point [6] and boiling point [7], and the boiling point parameters [8].

Here we have calculated the second virials for different temperatures using the correlations presented by Boushehri and Mason [4]. It has been shown that this procedure leads to an analytical EOS that can predict the saturated liquid density of cadmium, chromium, erbium, manganese, antimony, and zinc within ±4% up to hundreds of kelvins above the melting point.

2. THEORY

The starting point in the derivation of the ISM equation of state is the following equation that relates the pressure, P, to the pair distribution function $g(r)$ [9]:

$$\frac{P}{\rho kT} = 1 - (2\pi\rho/3kT)\int_0^\infty du\,(r)/dr\, g(r)r^3\, dr, \tag{1}$$

in which $u(r)$ is the pair potential as a function of distance r and k is the Boltzmann constant. Although the derivation of Eq. (1) assumes pairwise additivity for $u(r)$, many body effects can still be incorporated through the distribution function, $g(r)$.

Song and Mason, by the rearrangement of this equation reached a form in which the second virial coefficient, B_2, appears explicitly. Applying a division of the potential function similar to that of Weeks, Chandler, and Anderson [1, 10] and substituting the Carnahan and Starling formula [1, 11] for the pair distribution function at contact $g(d^+)$, in addition to some other approximations, gives the complete form of the ISM EOS:

$$\frac{P}{\rho kT} = 1 + \frac{(B-\alpha)\rho}{1+0.22\lambda b\rho} + \frac{\alpha\rho}{1-\lambda b\rho}. \tag{2}$$

where λ is an adjustable parameter.

If the values of B_2, α and b are known, the free parameter λ can be determined using a proper experimental datum point, which is found by a simple iterative procedure. Then the density at each temperature and pressure can be calculated by means of the cubic EOS. To determine the parameter, B_2, we have used the following correlation:

$$\begin{aligned} B_2(T)\rho_\mathrm{m} &= 0.403891 - 0.076484(\Delta H_\mathrm{vap}/RT)^2 \\ &\quad - 0.0002504(\Delta H_\mathrm{vap}/RT)^4. \end{aligned} \tag{3}$$

where ΔH_vap and ρ_m are the heat of vaporization and the density at the melting point which are very close to those of the triple point.

Boushehri and Mason [4] derived the following equations for $\alpha(T)$ and $b\ (T)$ by scaling:

$$\begin{aligned} b\rho_\mathrm{m} &= a_1\left[1 - c_1(RT/\Delta H_\mathrm{vap})\right]\exp\left[-c_1(RT/\Delta H_\mathrm{vap})\right] \\ &\quad + a_2\left\{1 - \left[1 + 0.25c_2(\Delta H_\mathrm{vap}/RT)^{1/4}\right]\right. \\ &\quad \left.\times \exp\left[-c_2(\Delta H_\mathrm{vap}/RT)^{1/4}\right]\right\}, \end{aligned} \tag{4}$$

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

with $a_1 = -0.1053$, $a_2 = 2.9359$, $c_1 = 5.7862$, $c_2 = 0.7966$.

3. RESULTS AND DISCUSSION

We have calculated the heat of vaporization at the melting point of cadmium, chromium, erbium, manganese, antimony, and zinc by means of the Clausius–Clapeyron equation from the temperature dependence of the vapor pressure of these metals [12]. ρ_m, T, P, and experimental density data for cadmium, chromium, erbium, manganese, and zinc have also been found in Ref. 12. The experimental density data for antimony were adopted from Ref. 13. Using this information, we calculated B_2, α and b by Eqs. (3)–(5). Then we calculated λ from a single P–ρ–T experimental datum point. Values obtained for λ as well as the heats of vaporization and liquid densities at the melting point of the metals are given in Table I.

Once the value of λ is determined, the densities of the liquid at different temperatures can be predicted by means of Eq. (2), which is cubic against ρ . So, the entire volumetric behavior of the liquid is established. We calculated the densities up to hundreds of kelvins above the melting point, the range that we could find experimental data for comparison. The results and the deviation percents are listed in Table II. Although the results listed in Table II show the degree of consistency between our model and experimental data, the results for zinc as a typical example are also shown in Fig. 1, on which any deviation pattern is more obvious.

This work shows that the ISM EOS can be applied to predict the PVT behavior of a number of metals, given above. Also it shows that the extrapolation of normal fluids' corresponding states correlations to the metallic region does not affect the final results. It may be due to the compensating effect made by the adjusting parameter λ. It should be noted that the best results are achieved for metals with relatively high vapor pressures.

Table I. Parameters for Different Metals

Metal	T_m(K)	$\rho_m(\mathrm{mol \cdot L^{-1}})$	$\Delta H_{vap}(\mathrm{J \cdot mol^{-1}})$	λ
Sb	903.8	31.24	1301.2	0.454
Cd	594	71.14	1008.8	0.461
Cr	2180	121.15	3436.7	0.464
Er	1802.5	52.96	2583.9	0.459
Mn	1519	108.30	2334.6	0.472
Zn	693	100.50	1148.5	0.462

Table II. Calculated Results for the Saturated Liquid Density of Metals Compared with Experiment

		Density $(\mathrm{mol \cdot L^{-1}})$		
T(K)	P(bar)	Calc.	Expt.	Dev. (%)
Antimony				
903.78	1.59×10^{-4}	31.23	30.88	−0.52
1000	7.93×10^{-4}	30.94	30.58	0.02
1100	3.12×10^{-3}	30.50	30.26	0.16
Cadmium				
594	1.54×10^{-4}	70.44	71.07	−0.98
600	1.89×10^{-4}	70.43	69.99	−0.90
700	3.43×10^{-3}	69.99	68.91	−0.01
800	3.02×10^{-1}	68.99	67.82	0.11
Chromium				
2180	6.93×10^{-3}	118.88	121.15	−1.88
2200	8.25×10^{-3}	118.84	120.73	−1.56
2300	1.89×10^{-2}	118.61	118.62	0.00
2400	4.03×10^{-2}	118.30	116.50	1.54
Erbium				
1802.5	4.68×10^{-4}	52.28	52.96	−1.29
1900	1.19×10^{-3}	52.05	52.04	0.01
2000	2.81×10^{-3}	51.75	51.10	1.27
2100	6.12×10^{-3}	51.40	50.17	2.46
Manganese				
1519	1.52×10^{-3}	104.34	108.30	−3.65
1600	3.91×10^{-3}	104.06	106.31	−2.12
1700	1.11×10^{-2}	103.58	103.86	−0.27
1800	2.79×10^{-2}	102.94	101.40	1.52
1900	6.38×10^{-2}	102.16	98.94	3.26
Zinc				
693	2.17×10^{-4}	99.25	100.47	−1.21
700	2.66×10^{-4}	99.24	100.36	−1.11
800	3.30×10^{-3}	98.68	98.67	0.00
900	2.35×10^{-2}	97.52	96.99	0.54
1000	1.13×10^{-1}	95.82	95.31	0.53

In summary, only two characteristic constants, the heat of vaporization and the liquid density at the melting point, are needed to predict the liquid densities of these metals without a knowledge of the exact potential energy function or the experimental second virial coefficients.

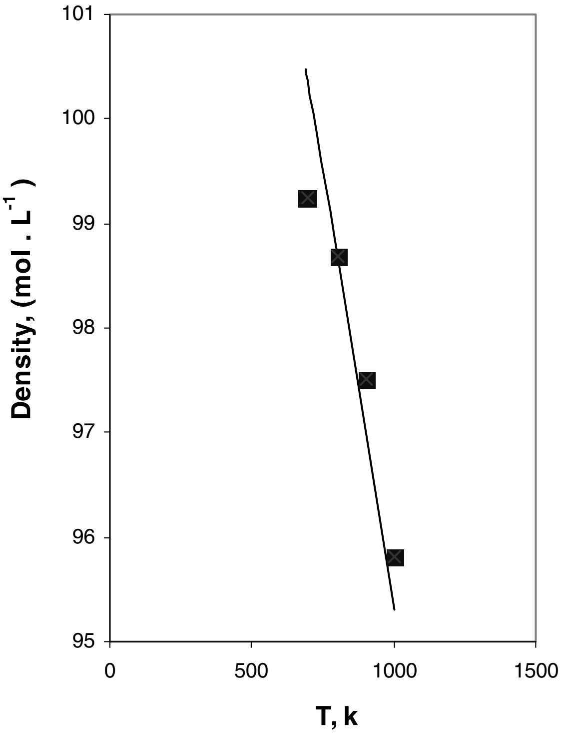

Fig. 1. Comparison of calculated (■) and experimental (—) saturated liquid density of zinc vs. temperature.

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REFERENCES

1. Y. Song and E. A. Mason, *J. Chem. Phys.* **91**:7840 (1989).
2. G. Ihm, Y. Song, and E. A. Mason, *J. Chem. Phys.* **94**:3839 (1991).
3. F. M. Tao and E. A. Mason, *Int. J. Thermophys.* **13**:1053 (1992).
4. A. Boushehri and E. A. Mason, *Int. J. Thermophys.* **14**:685 (1993).
5. S. Sheikh, M. M. Papari, and A. Boushehri, *Indust. Eng. Chem. Res.* **41**:3247 (2002).
6. M. H. Ghatee and A. Boushehri, *Int. J. Thermophys.* **17**:945 (1996).
7. N. Mehdipour and A. Boushehri, *Int. J. Thermophys.* **19**:331 (1998).
8. H. Eslami, *Int. J. Thermophys.* **21**:1123 (2000).
9. D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976).

10. J. D. Weeks, D. Chandler, and H. C. Anderson, *J. Chem. Phys*. **54**:5237 (1971).
11. N. F. Carnahan and K. E. Starling, *J. Chem. Phys*. **51**:635 (1969).
12. D. R. Lide, ed., *CRC Handbook of Chemistry and Physics* (CRC Press, New York, 2000); P. M. Nasch and S. G. Stein Emann, *Phys. Chem. Liq.* **29:**43 (1995).
13. L. Wang, Q. Wang, A. Xian, and K. Lu, *J. Phys. Condens.*: *Matter* **15:**777 (2003).