International Journal of Thermophysics, Vol. 19, No. 1, 1998

Equation of State for Molten Alkali Metals from Surface Tension. Part II

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Received September 10, 1997

This work presents a new method for predicting the equation of state for molten alkali metals, based on statistical–mechanical perturbation theory from two scaling constants that are available from measurements at ordinary pressures and temperatures. The scaling constants are the surface tension and the liquid density at the boiling temperature (γ_b, ρ_b). Also, a reference temperature, T_{Ref}, is presented at which the product ($T_{Ref} T_b^{1/2}$) is an advantageous corresponding temperature for the second virial coefficient, $B_2(T)$. The virial coefficient of alkali metals cannot be expected to obey a law of corresponding states for normal fluids, because two singlet and triplet potentials are involved. The free parameter of the Ihm–Song–Mason equation of state compensates for the uncertainties in $B_2(T)$. The vapor pressure of molten alkali metals at low temperatures is very low and the experimental data for $B_2(T)$ of these metals are scarce. Therefore, an equation of state for alkali metals from the surface tension and liquid density at boiling temperature (γ_b, ρ_b) is a suitable choice. The results, the density of Li through Cs from the melting point up to several hundred degrees above the boiling temperature, are within 5%.

KEY WORDS: alkali metals; corresponding states; equation of state; surface tension.

1. INTRODUCTION

Characteristics of the alkali metals as heat-transfer agents and reactor coolants have been noted many times [1, 2]. Nonhydrogenous primary coolants are required for intermediate and fast reactors, and liquid metals are of prime interest. Their advantages are a result of the metallic characteristics,

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little degradation in neutron flux, high boiling point, extended liquid range, high thermal conductivity, low vapor pressure, and high heat of vaporization. High power/weight ratios require heat transfer and working fluids with the characteristics of alkali metals. Radiator weight for heat rejection is a large factor in space power-plant design; the alkali metals permit heat rejection at high temperatures, with a resultant decrease in radiator area and weight. Alkali metals have application to high-temperature industrial processes where management of heat is facilitated by the high-temperature range over which metal is in the liquid state, together with its low pressure and good heat-transfer properties [2]. Considering the extensive industrial applications of alkali metals, the existence of an equation of state for molten alkali metals for predicting their thermophysical properties at high temperatures and pressures is necessary. The equilibrium thermodynamic properties of alkali metals have not been investigated widely because of the difficult experimental conditions, that is, high temperatures and low vapor pressures.

Metals, in particular, alkali metals in liquid and gaseous states can be treated as simple monatomic systems. Ewing et al. [3] have proposed a quasi-chemical equation of state based on the fact that the vapor state of these metals is composed of partial monatomic and higher-order molecular species. Monomers of alkali metals can interact by two possible singlet- and triplet-type potentials. Values of the second virial coefficient, which is the basic parameter in studying equilibrium thermodynamic properties, are not available over an appreciable range of temperature and there is no agreement between theory and experiment, where it is applicable. Nieto de Castro et al. [4] and Fialho et al. [5] have conducted series of calculations of equilibrium and transport properties for monatomic systems of alkali metal vapors, respectively. They argued that the interpretation of experimental data for thermophysical properties of alkali metal vapors is complicated by the formation of dimers even at low pressures. In circumstances where the experimental data for the second virial coefficient are scarce and theoretical calculations are not in reasonable agreement with experimental data, prediction of the thermophysical properties is an alternative to remedy the experimental difficulties [6]. Considering the recent advances in statistical–mechanical theories, we are able to predict the physical properties of the compressed normal liquids, their mixtures, and molten alkali metals [7]. This work presents a procedure for predicting the equation of state for molten alkali metals from properties that are readily available at ordinary pressures and temperatures. Here we use the surface tension and the liquid density at the boiling point as scaling parameters that can correlate and predict the thermophysical behavior of molten alkali metals over a wide range of temperatures and pressures.

2. THEORY

In this method, we use the theoretical equation of state presented by Ihm, Song, and Mason [8], which is based on statistical-mechanical perturbation theory for condensed fluids:

$$\frac{P}{\rho KT}=1+\frac{(B_2-\alpha)}{1+0.22\lambda}+\frac{\alpha\rho}{1-\lambda b\rho} \tag{1}$$

where ρ is the number (molar) density, kT has its usual meaning, B_2 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_2, α, and b are related to the intermolecular potentials by integrations, and λ is a constant. We can write the corresponding-states results in the form

$$G(b\rho)^{-1}=\alpha\rho\left[Z-1+\frac{(\alpha-B_2)\,\rho}{1+0.22\lambda b\rho}\right]^{-1}=1-\lambda b\rho \tag{2}$$

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., its graph *vs* $b\rho$ is a straight line, and also, λ is the absolute value of the slope of $G(b\rho)^{-1}$ *vs* $b\rho$. From the P–V–T data together with the values of α, b, and B_2, λ can be calculated. We show that using Eq. (1) as the equation of state for alkali metals can utilize the surface tension as an input datum which also depends on the potential energy.

3. CORRELATION PROCEDURE

Here we use the surface tension as a scaling constant for the calculation of $B_2(T)$, $\alpha(T)$, and $b(T)$ in Eq. (1). As a matter of fact, the surface tension is a measure of the cohesive energy density and the ranges of the effective forces are not larger than the molecular dimension [9, 10]. A desirable form of the energy function is $\gamma\rho^{-2/3}N^{1/3}/RT$, where γ is the surface tension, ρ is the molar liquid density, and N is Avogadro's number. Compared with the thermal energy, the reduced form of the function with the boiling point as a reference temperature takes the form $\gamma_b\rho_b{}^{-2/3}N^{1/3}/RT$. The term $\gamma_b\rho_b{}^{-2/3}N^{1/3}/RT$ is referred to as T_{Ref} [11]. Apparently the shape effects described by λ, the acentric factor, affect γ_b and ρ_b in such a way as to tend to compensate for their influence on $B_2(T)$. Here it is proposed that the boiling temperature, T_b, which appears to be a corresponding temperature for alkali metals, is a suitable choice. This choice can be further justified by noting that T_{Ref} contains the surface tension and the liquid density at the boiling temperature. In fact, for alkali metals T_{Ref} and T_{b} are readily available. Empirically we found that the product $(T_{\mathrm{Ref}} T_{\mathrm{b}}^{1/2})$ is an excellent characteristic temperature for molten alkali metals [11].

Both the heat of vaporization and the surface tension represent the cohesive energy density. Here we have calculated the quasi-second virial coefficient of alkali metals using Boushehri and Mason's correlation [12], with the heat of vaporization and the liquid density at the freezing point as scaling constants, to construct the following correlation:

$$B_2 \rho_{\mathrm{b}} = 0.11256 - 2.98032 T^{*-1} - 11.98358 T^{*-2} + 10.40116 T^{*-3} - 4.68916 T^{*-4} \quad (3)$$

shown in Fig. 1, where T^* has the same form as in the previous work [6] and is defined as

$$T^* = [T^{3/2} / T_{\mathrm{Ref}} T_{\mathrm{b}}^{1/2}]^{3/4} \quad (4)$$

where T_{Ref} is a reference temperature.

We used the tabulations of Vargaftik [13] and Adamson [14] for the liquid densities and surface tension, respectively, to construct the correlation

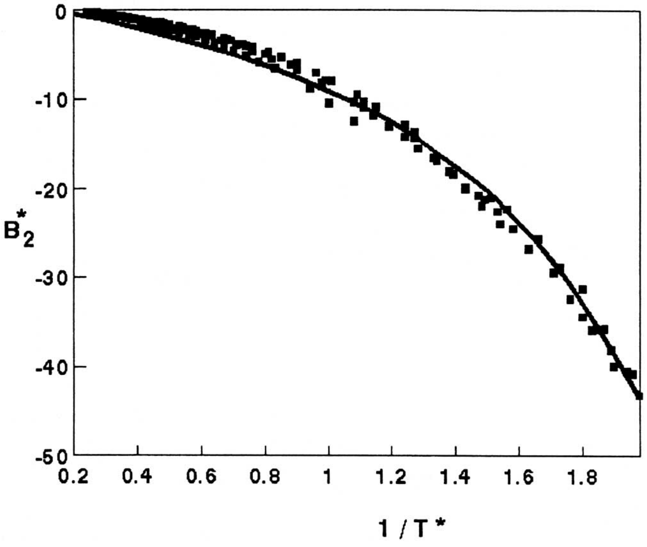

Fig. 1. B_2^*, $B_2\rho_{\mathrm{b}}$, vs $1/T^*$ for alkali metals. Due to the overlap of the reduced quasi-second virial coefficients, the same marker was used. The solid line represents the polynomial fit.

Eq. (3). We obtained the α and b parameters from the following equations by the relationship of Song and Mason [7]

$$\alpha \rho_b = a_1[\exp(-c_1 T^*)] + a_2[1 - \exp(c_2/T^{*1/4})] \quad (5)$$

$$b\rho_b = a_1(1 - c_1 T^*)[\exp(-c_1 T^*)] + a_2\{1 - (1 + 0.25c_2/T^{*1/4}) \exp(-c_2/T^{*1/4})\} \quad (6)$$

where

$$a_1 = -0.01504, \qquad c_1 = 0.7613$$

$$a_2 = 2.9387, \qquad c_2 = 1.3227$$

The characteristic free parameter of the alkali metals in the equation of state, λ, can be calculated from the two scaling constants at boiling temperature (γ_b and ρ_b) in a single iteration because it is just a correction factor.

4. RESULTS AND DISCUSSION

The main propose of this work was to develop an equation of state for molten alkali metals. Considering that experimental data for the second virial coefficient of these metals are scarce, the development of a suitable equation of state for molten alkali metals is necessary.

Comparison of our results with the previous work [6] (Fig. 2) shows that the choice of the surface tension as a scaling constant is better than the heat of vaporization for molten alkali metals. Because of this, determination of the equation of state for alkali metals from surface tension is a suitable method. Also, the results show that the choice of the boiling point as a scaling parameter (γ_b, ρ_b) is a suitable choice, because the vapor pressures of the alkali metals at the melting point and at low temperatures are very low. Therefore, we adopt the boiling temperature as our reference. It should be emphasized that this is not a crucial choice, merely a convenient one.

Using P–T data [13], we have calculated the density of Li, Na, K, Rb, and Cs. 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 present work also shows to what extent the results for alkali metals can be extended, namely, from the melting point up to

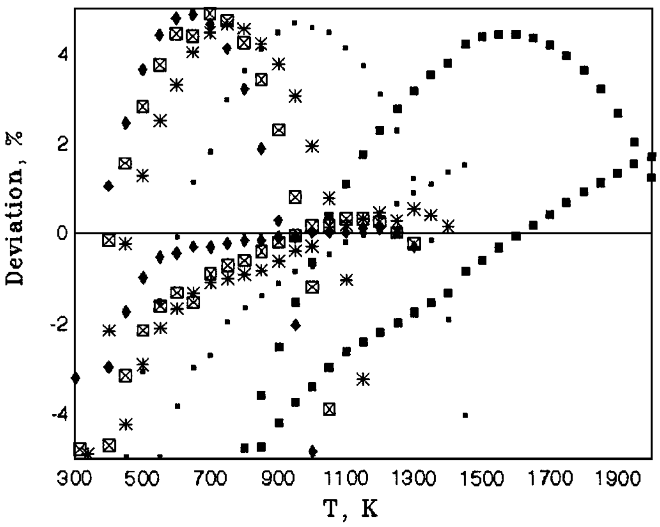

Fig. 2. Deviation plot for the density of lithium (■), sodium (▪), potassium (∗), rubidium (☒), and cesium (◆). The more highly deviated series are from the previous work [6], and the others are from the present work.

Table I. Density of Alkali Metals

T (K)	P (bar)	ρ_{ex} (mol · L^{-1})	ρ_{cal} (mol · L^{-1})	Dev. (%)
		Li		
850	3.723×10^{-5}	68.88	65.62	−4.73
900	1.242×10^{-4}	68.16	65.30	−4.19
950	3.645×10^{-4}	67.44	64.91	−3.75
1000	9.598×10^{-4}	66.72	64.45	−3.40
1050	2.301×10^{-3}	65.85	63.95	−2.96
1100	5.09×10^{-3}	65.13	63.42	−2.62
1150	1.051×10^{-2}	64.41	62.86	−2.40
1200	2.040×10^{-2}	63.69	62.29	−2.19
1250	3.752×10^{-2}	62.97	61.72	−1.98
1300	6.583×10^{-2}	62.25	61.15	−1.76
1350	0.1108	61.53	60.58	−1.54
1400	0.1794	60.81	60.01	−1.31
1450	0.2810	59.94	59.44	−0.83
1500	0.4269	59.22	58.87	−0.59
1550	0.6310	58.50	58.31	−0.32
1600	0.9102	57.78	57.74	−0.07
1650	1.283	57.06	57.16	0.17
1700	1.771	56.34	56.58	0.42
1750	2.399	55.62	56.00	0.68

Table I. (*Continued*)

T (K)	P (bar)	ρ_{ex} (mol·L^{-1})	ρ_{cal} (mol·L^{-1})	Dev. (%)
1800	3.191	54.90	55.40	0.91
1850	4.179	54.18	54.79	1.12
1900	5.397	53.46	54.18	1.34
1950	6.871	52.74	53.56	1.55
2000	8.639	52.02	52.92	1.73
		Na		
550	8.880×10^{-6}	38.54	36.63	−4.95
600	5.749×10^{-5}	38.02	36.56	−3.84
650	2.781×10^{-4}	37.49	36.37	−2.99
700	1.071×10^{-3}	37.10	36.09	−2.72
750	3.432×10^{-3}	36.45	35.73	−1.97
800	9.493×10^{-3}	35.93	35.34	−1.64
850	2.328×10^{-2}	35.41	34.92	−1.38
900	5.154×10^{-2}	34.88	34.49	−1.11
950	0.1049	34.36	34.07	−0.84
1000	0.1986	33.88	33.63	−0.74
1050	0.3535	33.36	33.20	−0.48
1100	0.5965	32.84	32.77	−0.21
1150	0.9607	32.32	32.34	−0.06
1200	1.504	31.80	31.91	0.34
1250	2.244	31.27	31.47	0.64
1300	3.216	30.75	31.02	0.88
1350	4.563	30.23	30.57	1.10
1400	6.256	29.71	30.11	1.35
1450	3.383	29.19	29.63	1.51
		K		
450	3.209×10^{-6}	20.51	19.64	−4.24
500	3.128×10^{-5}	20.20	19.61	−2.92
550	1.992×10^{-4}	9.90	19.48	−2.11
600	9.258×10^{-4}	9.62	19.29	−1.68
650	3.380×10^{-3}	9.31	19.05	−1.35
700	1.022×10^{-2}	9.00	18.79	−1.10
750	2.658×10^{-2}	8.70	18.51	−1.02
800	6.116×10^{-2}	8.41	18.24	−0.92
850	0.1274	18.11	17.96	−0.83
900	0.2441	17.80	17.69	−0.62
950	0.4357	17.49	17.42	−0.40
1000	0.7322	17.19	17.14	−0.30
1050	1.217	16.85	16.87	0.26
1100	1.864	16.55	16.58	0.18
1150	2.745	16.24	16.29	0.31
1200	3.913	15.93	16.00	0.44
1250	5.415	15.65	15.69	0.26

Table I. (*Continued*)

T (K)	P (bar)	ρ_{ex} (mol · L^{-1})	ρ_{cal} (mol · L^{-1})	Dev. (%)
1300	7.304	15.29	15.37	0.52
1350	9.628	14.98	15.04	0.40
1400	12.44	14.68	14.70	0.14
		Rb		
400	1.690×10^{-6}	16.75	15.96	−4.71
450	2.230×10^{-5}	16.47	15.95	−3.15
500	1.733×10^{-4}	16.21	15.86	−2.16
550	9.194×10^{-4}	15.95	15.69	−1.63
600	3.664×10^{-3}	15.68	15.47	−1.33
650	1.174×10^{-2}	15.48	15.24	−1.55
700	3.174×10^{-2}	15.14	15.00	−0.92
750	7.493×10^{-2}	14.87	14.76	−0.74
800	0.1584	14.60	14.51	−0.61
850	0.3059	14.33	14.27	−0.42
900	0.5476	14.06	14.03	−0.21
950	0.9206	13.79	13.78	−0.07
1000	1.467	13.52	13.54	0.14
1050	2.241	13.26	13.28	0.15
1100	3.295	12.98	13.02	0.31
1150	4.684	12.71	12.75	0.31
1200	6.466	12.44	12.47	0.24
1250	8.698	12.17	12.17	0.00
1300	11.43	11.90	11.87	−0.25
		Cs		
400	3.825×10^{-6}	13.40	13.00	−2.98
450	4.435×10^{-5}	13.19	12.96	−1.74
500	3.110×10^{-4}	12.97	12.84	−1.00
550	1.517×10^{-3}	12.75	12.68	−0.55
600	5.646×10^{-3}	12.54	12.48	−0.47
650	1.708×10^{-2}	12.32	12.28	−0.32
700	4.395×10^{-2}	12.11	12.07	−0.33
750	9.954×10^{-2}	11.89	11.86	−0.25
800	0.2029	11.68	11.66	−0.17
850	0.3798	11.47	11.45	−0.17
900	0.6622	11.25	11.24	−0.09
950	1.086	11.04	11.03	−0.09
1000	1.693	10.82	10.82	0.00
1050	2.527	10.59	10.59	0.00
1100	3.629	10.36	10.36	0.00
1150	5.038	10.11	10.12	0.09
1200	6.790	9.86	9.87	0.10
1250	8.889	9.61	9.61	0.00
1300	11.41	9.36	9.33	−0.32

Table II. Parameters of the Metals

Metal	T_b (K)	γ_b ($J \cdot m^{-2}$)	ρ_b ($mol \cdot L^{-1}$)	λ
Li	1615.0	0.2351	57.5677	0.396
Na	1151.2	0.1199	32.3343	0.400
K	1032.2	0.0631	16.9693	0.391
Rb	959.0	0.0500	13.7431	0.390
Cs	943.0	0.0405	11.0675	0.385

several hundred degrees above the boiling temperature, the results are within 5%.

The values of λ for the alkali metals are given in Table II. Although it is a free parameter that incorporates the inaccuracy associated with the temperature-dependent constants too, it is in accordance with the earlier finding of a linear relationship for the corresponding-states function, $G(b\rho)^{-1}$. Also, the values of λ incorporate the quantum effects of Li and Na [6].

The second virial coefficient of alkali metals cannot obey a law of corresponding states with normal fluids because alkali metals have the unfavorable characteristics of interacting through the singlet and triplet potential so that the treatment by a single potential here is fortuitous. In this way we get an estimate of the second virial coefficient of alkali metals over the entire range of temperatures to be used in Eq. (3). This is of special interest since no experimental data at low temperatures are available.

In summary, the present work indicates that the physical properties can be predicted from just two scaling constants, the surface tension and the liquid density at boiling temperature, which can be readily measured. Determination of the equation of state for molten alkali metals from surface tension with respect to the second virial coefficients, which are experimentally scarce, gives excellent results that are within 5%.

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