International Journal of Thermophysics, Vol. 16, No. 6, 1995

An Analytical Equation of State for Molten Alkali Metals

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Received November 4, 1994

This paper brings the molten alkali metals into the scope of a new statistical mechanical equation of state that is known to satisfy normal fluids over the whole range. As for normal fluids, the latent heat of vaporization and density at freezing temperature are the only inputs (scaling factors). The corresponding-states correlation of normal fluids is used to calculate the second virial coefficient, $B_2(T)$, of alkali metals, which is scarce experimentally and its calculation is complicated by dimer formation. Calculations of the other two temperature-dependent constants, $\alpha(T)$ and $b(T)$, follow by scaling. The virial coefficients of alkali metals cannot be expected to obey a law of corresponding states for normal fluids. The fact that two potentials are involved may be the reason for this. Thus, alkali metals have the characteristics of interacting through singlet and triple potentials so that the treatment by a single potential here is fortuitous. The adjustable parameter of the equation of state, Γ, compensates for the uncertainties in $B_2(T)$. The procedure used to calculate the density of liquids Li through Cs from the freezing line up to several hundred degrees above the boiling temperatures. The results are within 5%.

KEY WORDS: cohesive energy; equation of state; molten alkali metals; statistical mechanics.

1. INTRODUCTION

A knowledge of P–V–T behavior of molten metals is required for the assessment of various aspects of metallurgical and processing operations. Because of their high heats of vaporization alkali metals, in particular, are of special interest in that they can be used in nuclear power plants and other heat transfer processes, as coolants at high temperatures and

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pressures. Their equilibrium thermodynamic properties have not been investigated widely because of the difficult experimental conditions, i.e., high temperatures and low vapor pressures.

Metals in liquid and gaseous states 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 [1], equation of state [2], and law of rectilinear density [3, 4] are applied. In particular, alkali metals have been investigated and Ewing et al. [2] have proposed a quisichemical equation of state based on the fact the vapor state of these metals is composed of partial monatomic and higher-order molecular species. Other efforts involve NRL virial equations of state of vapor [2] and analytical equations of state for the liquid state [5].

Monomers of alkali metals can interact by two possible singlet- and triplet-type potentials. The variety of the degree of dimerization and higher-order polyatoms among the metals of the group makes them a complex set to be treated by the same potential function. Values of the second virial coefficient, which is the main parameter in studying the 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. Sannigrahi et al. [6] have used the Morse and Rydberg potential functions to calculate the total second virial coefficient from the manifold of singlet and triplet ground electronic states of the dimer. The results roughly compare with the *P–V–T* data of Na, K, and Cs vapors that have been reported (for high temperatures only) in the literature. Nieto de Castro et al. [7] and Fialho et al. [8, 9] 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. It follows that the calculations for monatomic species should produce independent information for the zero-density limits of the experimental properties [7–9].

In the circumstances where the experimental data for the second virial coefficient are scarce and theoretical calculations are not in a reasonable agreement with experimental data, prediction of thermodynamic properties is an alternative to remedy the experimental difficulties. The main purpose of the present work is to extend previous applications of statistical mechanical equations of state [10, 11] to include alkali metals in the liquid state.

With the recent advancement in statistical mechanical theories, the physical behavior of the liquid state of matter can be considered more extensively. The new analytical equation of state based on statistical mechanical perturbation theory [12] predicts accurate physical properties for both spherical and molecular fluids. The equation is shown to be good in that it can be used to predict the thermodynamic properties of compressed liquids from the freezing line up to the critical point without applying the critical parameters or acentric factors. Knowing the intermolecular potential function, one can calculate the second virial coefficient, $B_2(T)$, as one of the parameters of the equation of state. The other two temperature-dependent constants in the equation of state that can be calculated by integration are $\alpha(T)$, which takes care of the softness of the potential function and is equivalent to the contribution of the repulsive side of the potential function to $B_2(T)$, and $b(T)$ which is the analogue of the van der Waals covolume. The Carnahan–Starling equation of state has been adopted in the equation as $G(b\rho)$. $G(b\rho)^{-1}$ is a linear function of $b\rho$ only and, in its final form [Eq. (2), Section 2], demonstrates a principle of corresponding states [10]. The results are remarkably good when applied to Lennard–Jones (12–6) liquids.

In this paper, we present a procedure for the establishment of temperature-dependent parameters for alkali metals to be used in the equation of state. This could be done by using two scaling constants, the cohesive energy density at the boiling and the density at the triple point. The monomers of metals in the vapor state interact through singlet- and triplet-type potentials, but the present results show that the treatment by a single Lennard–Jones (12–6) potential to calculate temperature-dependent constants of the equation of state, $\alpha(T)$ and $b(T)$, applies to alkali metals quite well. This indicates neither that the dual nature of forces is contradictory nor that Lennard–Jones (12–6) model is the best potential function for alkali metals in vapor state.

It should be considered that the cohesive energy density obtained from vapor–pressure data does not alter the equation of state due to the formation of polyatoms in the metallic vapor, because it is assumed that the structure of the vapor is ordered with temperature (of boiling). It is evident just by argument.

2. EQUATION OF STATE

We summarize the results of derivation of the statistical mechanical equation of state, while the details can be found elsewhere [12–14]. The equation of state is

$$P/\rho RT = 1 - (\alpha - B_2)\,\rho/(1 + 0.22\Gamma b\rho) + \alpha\rho G(b\rho) \tag{1}$$

where

$$G(b\rho) \approx 1/(1 - \Gamma b\rho) \tag{2}$$

and P is the pressure, ρ is the molar density, RT is the thermal energy per mole at temperature T, B_2 is the second virial coefficient, α is the contribution of repulsive side of the potential function to B_2, and b is the analogue of the van der Waals covolume. $G(b\rho)$ is the average effective pair distribution function at contact for equivalent hard convex bodies. It is a function of $b\rho$ only and $G(b\rho)^{-1}$ versus $b\rho$ is linear over the whole range from the freezing line up to the critical point with a slope of Γ, depending on the particular substance. α and b are related by $b = \alpha + T(d\alpha/dT)$. From the P–V–T data together with the value of α, b, and B_2, Γ can be calculated by successive approximation in accordance to Eq. (1). For noble gases, the value of Γ at the triple point equals 0.381. This parameter along with other parameters is one of the constants that characterizes a particular system. The P–V–T data collapse to a single line with slope Γ when $G(b\rho)^{-1}$ is plotted versus $b\rho$.

If the details of the potential are known, $B_2(T)$, $\alpha(T)$, and $b(T)$ can be calculated by integration. Different potential functions have already been tried [14]. Although the Aziz potential functions [14, 15] are known to be the most accurate for noble gases, but for most practical purposes, the Lennard–Jones (12–6) potential works adequately. Thus, in practice, either $B_2(T)$ can be calculated from Boyle's volume and Boyle's temperature or, if available, its experimental value can be used.

3. ALKALI METALS

For alkali metals, neither an accurate potential functions nor experimental values of $B_2(T)$ over the whole range of temperatures are known. Instead we propose that the $B_2(T)$ values be calculated from a corresponding-states correlation with normal fluids [10, 11]. At this point we are not concerned with the uncertainties in $B_2(T)$, because the adjustable parameter of the equation of state, Γ, compensates for the associated uncertainties. The only two constants in the correlation are the density at the triple point, ρ_{tr}, and the cohesive energy, which is likely to be substituted by latent heat of vaporization, ΔH_{v}. In the correlation [10]

$$B_2^*(T) = B_2(T)\,\rho_{\text{tr}} = A + B(\Delta H_{\text{v}}/RT)^2 + C(\Delta H_{\text{v}}/RT)^4 \tag{3}$$

with

$$A = 0.403891, \qquad B = -0.076484, \qquad C = -0.0002504$$

Once the $B_2(T)$ values are known, the calculation of $\alpha(T)$ and $b(T)$ follows from the scaling constants. This can be done since $\alpha(T)$ and $b(T)$ are rather insensitive to the details of the shape of the potential function. Using the data for Lennard–Jones (12–6) potential, Boushehri and Mason [10] have obtained the following expressions:

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

$$b\rho_{\mathrm{tr}} = a_1[1 - c_1(RT/\Delta H_{\mathrm{v}})]\exp[-c_1(RT/\Delta H_{\mathrm{v}})] + a_2\{1 - [1 + 0.25c_2(\Delta H_{\mathrm{v}}/RT)^{1/4}]\}\exp[-c_2(\Delta H_{\mathrm{v}}/RT)^{1/4}] \quad (5)$$

with

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

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

Using ΔH_{v} and ρ_{tr} data, in the final step, we calculate the value of Γ using Eqs. (3), (4), (5), and (1), respectively, as the constant that characterizes the equation of state of a particular system. For the calculation of Γ, a single iteration at the triple point is sufficient because it is just a correction factor.

4. RESULTS AND DISCUSSION

Although the uncertainty associated with extrapolation cannot be ruled out, the corresponding-states correlation for calculating the second virial coefficient is of great value since the extrapolation to the metallic region yields parameters of the analytical equation of state. The second virial coefficients of alkali metal cannot expected to obey a law of corresponding states with normal fluids. The fact that two potentials are involved makes this almost impossible. In other words, alkali metals have the unfortunate characteristics of interacting through singlet and triplet potentials so that the treatment by single potential here is fortuitous. The observation here can be interpreted that all metals of the group obey nearly the same two-parameter intermolecular pair potential energy functions of singlet and triplet, from which a weighted average (of singlet and triplet) second virial coefficient can be calculated [6, 7, 16]. Again, we emphasis that Γ incorporates any uncertainties in the calculated $B_2(T)$ values. In this way we get an estimate of the second virial coefficient of alkali metals vapor over the entire range of temperature to be used in Eq. (1). This is of special interest since no experimental data at low temperatures are available. It is worth noting that the correlation is a basis to simplify the calculation by avoiding the use of an intermolecular potential function, which is complicated due to the dimer formation.

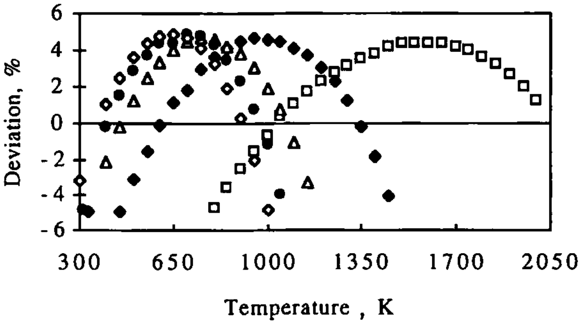

Fig. 1. Deviation plot for density of alkali metals. The points are (□) lithium, (◆) sodium, (△) potassium, (●) rubidium, and (◇) cesium.

Two vapor-pressure data points, to calculate the heat of vaporization, and the density at the triple point are sufficient to estimate the thermodynamic properties from near-freezing temperature up to several hundred degrees above the boiling temperature. Using P–T data [17], we have calculated the density of Li, Na, K, Rb, and Cs and the results are shown in Table I. In metals, although the interatomic potentials are inherently different in the liquid and vapor states, the Eq. (1) with the Lennard–Jones (12–6) potential used to calculate $\alpha(T)$ and $b(T)$ still produces results within reasonable accuracy (of 5%). This can be attributed to the fact that $\alpha(T)$ and $b(T)$ do not depend on the details of the potential function. The plot in Fig. 1 shows the deviation in density for alkali metals as predicted by the present procedure.

Table I. The Physical Properties of Molten Alkali Metals: Columns 3 and 4 Give the Calculated and Experimental Densities, Respectively

T (K)	P (bar)	Density (mol · L^{-1}) Calc.	Density (mol · L^{-1}) Expt.	Dev. (%)
		Lithium		
800	9.572×10^{-6}	66.44	69.60	−4.76
850	3.723×10^{-5}	66.49	68.88	−3.59
900	1.242×10^{-4}	66.49	68.16	−2.51
950	3.645×10^{-4}	66.42	67.44	−1.54
1000	9.598×10^{-4}	66.28	66.72	−0.66
1050	2.301×10^{-3}	66.09	65.85	0.36
1100	5.090×10^{-3}	65.84	65.13	1.08

Table I. *(Continued)*

T (K)	P (bar)	Density ($mol \cdot L^{-1}$) Calc.	Expt.	Dev. (%)
1150	1.051×10^{-2}	65.55	64.41	1.74
1200	2.040×10^{-2}	65.17	63.69	2.27
1250	3.752×10^{-2}	64.76	62.97	2.77
1300	6.583×10^{-2}	64.29	62.25	3.16
1350	0.1108	63.78	61.53	3.53
1400	0.1794	63.21	60.81	3.80
1450	0.2810	62.59	59.94	4.23
1500	0.4269	61.93	59.22	4.38
1550	0.6310	61.22	58.50	4.44
1600	0.9102	60.47	57.78	4.44
1650	1.283	59.67	57.06	4.37
1700	1.771	58.82	56.34	4.21
1750	2.399	57.92	55.62	3.97
1800	3.191	56.98	54.90	3.65
1850	4.179	55.98	54.18	3.21
1900	5.397	54.94	53.46	2.69
1950	6.871	53.84	52.74	2.04
2000	8.639	52.68	52.02	1.25
		Sodium		
450	5.902×10^{-8}	37.67	39.54	−4.96
500	9.363×10^{-7}	37.86	39.02	−3.06
550	8.880×10^{-6}	37.96	38.54	−1.53
600	5.749×10^{-5}	37.98	38.02	−0.11
650	2.781×10^{-4}	37.92	37.49	1.11
700	1.071×10^{-3}	37.78	37.10	1.80
750	3.432×10^{-3}	37.56	36.45	2.96
800	9.493×10^{-3}	37.28	35.93	3.62
850	2.328×10^{-2}	36.93	35.41	4.11
900	5.154×10^{-2}	36.52	34.88	4.49
950	0.1049	36.05	34.36	4.69
1000	0.1986	35.51	33.88	4.59
1050	0.3535	34.92	33.36	4.47
1100	0.5965	34.28	32.84	4.12
1150	0.9607	33.57	32.32	3.72
1200	1.504	32.81	31.80	3.10
1250	2.244	32.00	31.27	2.28
1300	3.216	31.12	30.75	1.19
1350	4.563	30.18	30.23	−0.17
1400	6.256	29.16	29.71	−1.89
1450	8.383	28.06	29.19	−4.03

Table I. *(Continued)*

T (K)	P (bar)	Density (mol · L^{-1}) Calc.	 Expt.	Dev. (%)
		Potassium		
336.4	1.370×10^{-9}	20.19	21.18	−4.90
400	1.837×10^{-7}	20.38	20.82	−2.16
450	3.209×10^{-6}	20.46	20.51	−0.25
500	3.128×10^{-5}	20.46	20.20	1.27
550	1.992×10^{-4}	20.41	19.90	2.49
600	9.258×10^{-4}	20.29	19.62	3.30
650	3.380×10^{-3}	20.12	19.31	4.03
700	1.022×10^{-2}	19.89	19.00	4.47
750	2.658×10^{-2}	19.61	18.70	4.64
800	6.116×10^{-2}	19.29	18.41	4.56
850	0.1274	18.91	18.11	4.23
900	0.2441	18.50	17.80	3.78
950	0.4357	18.04	17.49	3.05
1000	0.7322	17.53	17.19	1.94
1050	1.217	16.98	16.85	0.76
1100	1.864	16.38	16.55	−1.04
1150	2.745	15.73	16.24	−3.24
		Rubidium		
312.7	2.460×10^{-9}	16.54	17.33	−4.78
400	1.690×10^{-6}	16.72	16.75	−0.18
450	2.230×10^{-5}	16.73	16.47	1.55
500	1.733×10^{-4}	16.68	16.21	2.82
550	9.194×10^{-4}	16.57	15.95	3.74
600	3.664×10^{-3}	16.41	15.68	4.44
650	1.174×10^{-2}	16.19	15.48	4.39
700	3.174×10^{-2}	15.92	15.14	4.90
750	7.493×10^{-2}	15.61	14.87	4.74
800	0.1584	15.25	14.60	4.26
850	0.3059	14.84	14.33	3.43
900	0.5476	14.39	14.06	2.29
950	0.9206	13.90	13.79	0.79
1000	1.467	13.36	13.52	−1.20
1050	2.241	12.76	13.26	−3.91
		Cesium		
301.6	2.661×10^{-9}	13.39	13.82	−3.21
400	3.825×10^{-6}	13.54	13.40	1.04
450	4.435×10^{-5}	13.52	13.19	2.44
500	3.110×10^{-4}	13.46	12.97	3.64

Table I. *(Continued)*

T (K)	P (bar)	Density ($\mathrm{mol \cdot L^{-1}}$) Calc.	Density ($\mathrm{mol \cdot L^{-1}}$) Expt.	Dev. (%)
550	1.517×10^{-3}	13.34	12.75	4.42
600	5.646×10^{-3}	13.17	12.54	4.78
650	1.708×10^{-2}	12.95	12.32	4.86
700	4.395×10^{-2}	12.70	12.11	4.65
750	9.954×10^{-2}	12.40	11.89	4.11
800	0.2029	12.07	11.68	3.22
850	0.3798	11.69	11.47	1.88
900	0.6622	11.28	11.25	0.27
950	1.086	10.82	11.04	−2.03
1000	1.693	10.32	10.82	−4.84

It has been shown that the vapor of alkali metals is composed of polyatoms. Because the formation of polyatoms changes the vapor composition, a rectilinear density diameter has been questioned [2]. However, consistent liquid and vapor properties have been determined for several alkali metals over appreciable range of temperature, and it has been shown that the deviation from linearity is small [2]. Therefore it is assumed that the changing composition of vapor is ordered with temperature and it does not affect significantly the linearity of rectilinear density. In the present case, if we determine the molar heat of vaporization, ΔH_v, from vapor pressure data, we notice that, it does not correlate with the molar cohesive energy as stated previously. However, a normal equation of state would be obtained because ΔH_v is used in pair with T_b. This means that ΔH_v is ordered with vapor composition and thus with the corresponding temperature.

The values of Γ along with other parameters used in the equation of state are listed in Table II. The values of Γ for all the metals are nearly close to each other and this indicates that the structural complexities of all the metals that govern the thermophysical properties show similarities and thus group laws of corresponding states are applicable. Lithium deviates slightly probably due to quantum effects.

The validity of Eq. (1) for alkali metals is evident by the fact that (i) the equation of state could predict the physical properties within a reasonable range of accuracy and (ii) the $G(b\rho)^{-1}$ recognizes its role as a virtual strong corresponding states. This is a useful result for subcritical region.

Table II. The Parameters of the Metals

Metal	ΔH_v (kJ·mol^{-1})	ρ_{tr} (mol·m^{-3})	T_m (K)	T_b (K)	Γ
Li	151.203	75360.2	453.7	1615	0.517
Na	101.764	40362.6	371.0	1151	0.485
K	83.343	21176.5	336.4	1032	0.472
Rb	75.578	17325.7	312.7	959	0.473
Cs	71.841	13821.4	301.6	943	0.466

ACKNOWLEDGMENT

We are indebted to the Research Committee of Shiraz University for supporting this project.

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