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Equation of State for Molten Alkali Metal Alloys[1]

H. Eslami[2]

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Calculated results of the liquid density of binary molten alloys of Na–K and K–Cs over the whole range of concentrations and that of a ternary molten eutectic of Na–K–Cs from the freezing point up to several hundred degrees above the boiling point are presented. The calculations were performed with the analytical equation of state proposed by Ihm, Song, and Mason, which is based on statistical-mechanical perturbation theory. The second virial coefficients were calculated from the corresponding-states correlation of Mehdipour and Boushehri. Calculation of the other two temperature-dependent parameters was carried out by scaling. The calculated results cover a much wider range of temperatures and are more accurate than those presented in our previous work.

KEY WORDS: alkali metal alloys; cohesive energy; equation of state; statistical mechanics; surface tension.

1. INTRODUCTION

There is an increasing demand for a reliable and consistent set of thermodynamic data for alkali metals. This demand is based on their growing technical importance, due mainly to their specific advantages for high-temperature applications. Alkali metals act as working fluids for Rankine cycles, solar power plants, and magnetohydrodynamic power generation [1, 2]. The rapidly increasing fuel costs and need for improved thermal efficiency of power plants consequently led to an increase in the peak temperatures of the cycles.

Because of their wide range of applicability and simple electronic structure, liquid alkali metals have often been chosen as prototype elements for research, but there are temperature regions where accurate information

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[1] This paper is dedicated to Professor Ali Boushehri of Shiraz University.

[2] Department of Chemistry, College of Sciences, Persian Gulf University, Boushehr 75168, Iran.

on the thermodynamic properties does not exist. Prediction of these properties appears at present to be the only alternative to the experimental difficulties associated with their measurement.

Modern perturbation theories of liquids [3, 4] have been developed over the past 20 years based on the recognition that the structure of dense fluids is determined by the repulsive forces, so that fluids of hard bodies can serve as useful reference systems [5]. The influence of the attractive forces can then be treated by statistical–mechanical perturbation theory, as can the softness of repulsions. Given the intermolecular forces, it is now possible to predict thermodynamic properties of dense fluids from perturbation theories over their stable range of temperature and density.

The purpose of this paper is to present a method for predicting the equation of state of molten alkali metal alloys from properties that are readily available at ordinary pressures and temperatures. In particular, we use the surface tension and the liquid density at the boiling temperature as two scaling constants that have been shown to correlate and predict the behavior of molten alkali metals [6].

2. THEORY

We begin with the pressure equation and the assumption that the intermolecular potential is pairwise additive [7]:

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

where p is the pressure, ρ is the molar (number) density, kT is the thermal energy, $u(r)$ is the intermolecular pair potential, and $g(r)$ is the pair distribution function. Song and Mason [8] applied the perturbation theory of Weeks–Chandler–Andersen [4] and corrected for the attractive forces to obtain

$$\frac{p}{\rho kT} = 1 + B_2\rho + \alpha\rho[G(b\rho) - 1] \tag{2}$$

where B_2 is the second virial coefficient, α is a temperature-dependent parameter that scales for the softness of the repulsive forces, b is a temperature-dependent analogue of the van der Waals covolume related to α by $b = d(\alpha T)/dT$, and $G(b\rho)$ is the average pair distribution function at contact for equivalent hard nonspherical convex bodies. The parameters B_2, α, and b are related to the intermolecular potential by integrations.

A new strong principle of corresponding states is contained in Eq. (2), which led to an appreciable improvement in both accuracy and simplicity [9]. The basic idea is that the form of $G(b\rho)$ does not need to be specified according to some model of a fluid composed of hard convex bodies but that Eq. (2) can be solved for $G(b\rho)$ in terms of $Z \equiv p/(\rho RT)$, α, B_2, and ρ, all of which can be determined from experiment, and this particular combination of quantities is then predicted to be a function of the single variable $b\rho$. A whole p–v–T surface is thereby collapsed into a single curve by plotting the data in this special way. Plots of p–v–T data for a number of fluids showed that $G(b\rho)^{-1}$ verus $b\rho$ is a straight line with a slope that depends on the particular substance.

The preceding results culminate in the equation of state:

$$\frac{p}{\rho kT} = 1 - \frac{(\alpha - B_2)\,\rho}{1 + 0.22\lambda b\rho} + \frac{\alpha\rho}{1 - \lambda b\rho} \tag{3}$$

where λ is the absolute value of the slope of G^{-1} as a function of $b\rho$.

The formal extension of Eq. (3) to mixtures can be written in the form [10]

$$\frac{P}{\rho RT} = 1 + \rho \sum_{ij} x_i x_j (B_{ij} - \alpha_{ij} F_{ij}) + \rho \sum_{ij} x_i x_j G_{ij} \alpha_{ij} \tag{4}$$

where ρ is the total molar density, x_i and x_j are mole fractions, and the double summations run over all components of the mixture. The quantities F_{ij} and G_{ij} are given in Ref. 10.

The interaction parameters $(B_2)_{ij}$, α_{ij}, and b_{ij} for $i \neq j$ correspond to a hypothetical substance whose molecules interact according to a pairwise i–j potential. The purpose of this work is to use Eq. (4) for molten alkali metal alloys on the basis of minimal input information, that is, the surface tension and the liquid density at the boiling point.

3. THE TEMPERATURE-DEPENDENT PARAMETERS

A fundamental requirement for the theoretical calculation of the temperature-dependent parameters of the equation of state is a knowledge of sound reliable pair-potential energy functions for which any two atoms of the gas interact. For alkali metal vapors the problem reduces to that of obtaining the ground singlet and triplet potential energy curves. Previous calculations of $B_2(T)$ for alkali vapors consist of the values reported by Sinanoglu and Pitzer [11] for Na, by Davies et al. [12] for K, by Sannigrahi et al. [13] for the vapors of Li through Cs, and by Mies and

Julienne [14] and Holland et al. [15, 16] for Li and Na. All these authors, except the latter, based their calculations on either the Morse or the Rydberg functions to represent the singlet potential, which gives too much attraction at large internuclear separation and, hence, overestimates the absolute value of the second virial coefficient.

More recently Nieto de Castro et al. [17] used reliable analytical potentials for both the singlet and the triplet states of all the alkali homonuclear diatomic interactions proposed by Varandas et al. [18, 19] to calculate the second virial coefficient at temperatures from 600 to 3000 K. Their accurate calculations do not agree very well with the previous methods, especially at low temperatures, and they claim that the interpretation of experimental data on the thermophysical properties of alkali metals is complicated by the formation of dimers. Thus, there is seldom any accurate straightforward potential energy function for which the second virial coefficient and the other two temperature-dependent parameters can be calculated over a wide range of temperatures. However, $B_2(T)$ can be found experimentally, and $\alpha(T)$ and $b(T)$ can be calculated from $B_2(T)$ by means of simple two-constant scaling rules [20]. Unfortunately, the experimental values of $B_2(T)$ for alkali vapors are scarce.

In the circumstances where the experimental values of $B_2(T)$ or an accurate potential energy function for their calculations are not available, there are several correlation procedures (usually based on the law of corresponding states) by which $B_2(T)$ can be estimated with reasonable accuracy. The best of these requires three constants [21, 22]: the critical temperature, the critical pressure, and the Pitzer acentric factor. Boushehri and Mason [23] reduced the problem to finding at least two scaling constants available from simple measurements at ordinary temperatures and pressures, namely, the heat of vaporization and the liquid density at the triple point. Their method has been extended to molten alkali metals by Ghatee and Boushehri [24] and to molten alkali metal alloys by Eslami and Boushehri [25]. Mehdipour and Boushehri [6] have used the surface tension and the liquid density at the boiling temperature as two scaling constants to obtain the following correlation, which is superior to the previous one [24].

$$B_2\rho_b = 0.11256 - 2.98032T^{*-1} - 11.98358T^{*-2} + 10.40116T^{*-3} - 4.68916T^{*-4} \tag{5}$$

with

$$T^* = [T^{3/2}/T_{\text{Ref}}T_b^{1/2}]^{3/4} \tag{6}$$

and

$$T_{\mathrm{Ref}} = \gamma_{\mathrm{b}} \rho_{\mathrm{b}}^{-2/3} N^{1/3} / R \tag{7}$$

where γ_{b} and ρ_{b} are the surface tension and the liquid density at the boiling point, respectively, and N is Avogadro's number.

The calculation of the other two temperature-dependent parameters can be done by scaling using the Lennard–Jones (12–6) potential [6]:

$$\alpha \rho_{\mathrm{b}} = a_1[\exp(-c_1 T^*)] + a_2[1 - \exp(-c_2/T^{*1/4})] \tag{8}$$

$$b\rho_{\mathrm{b}} = a_1(1 - c_1 T^*)[\exp(-c_1 T^*)] + a_2[1 - (1 + 0.25c_2/T^{*1/4}) \times \exp(-c_2/T^{*1/4})] \tag{9}$$

where

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

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

The present correlation can be generalized to mixtures of any number of components, a result which would have great predictive power. The simplest combining rules for predicting unlike-molecule interactions from the like-molecule interactions are a geometric mean for γ and T and an arithmetic mean for r_{m}, the potential well-depth position, i.e.,

$$(\gamma_{\mathrm{b}})_{ij} = [(\gamma_{\mathrm{b}})_i (\gamma_{\mathrm{b}})_j]^{1/2} \tag{10}$$

$$(T_{\mathrm{b}})_{ij} = [(T_{\mathrm{b}})_i (T_{\mathrm{b}})_j]^{1/2} \tag{11}$$

and

$$(\rho_{\mathrm{b}})_{ij}^{-1/3} = \tfrac{1}{2}[(\rho_{\mathrm{b}})_i^{-1/3} + (\rho_{\mathrm{b}})_j^{-1/3}] \tag{12}$$

Once $(\gamma_{\mathrm{b}})_{ij}$ and $(\rho_{\mathrm{b}})_{ij}$ are known, the values of $(B_2)_{ij}$, α_{ij}, and b_{ij} follow from Eqs. (5)–(12) as for single substances.

4. COMPARISON WITH EXPERIMENT

We have used the tabulations of Vargaftik [26] and Adamson [27] for the liquid density and the surface tension at the boiling point, respectively, to calculate the temperature-dependent parameters of the equation of state with Eqs. (5)–(9). Knowing the values of the temperature-dependent parameters, it takes one experimental p–v–T datum point to calculate the free parameter of the equation of state. The values of λ so specified for

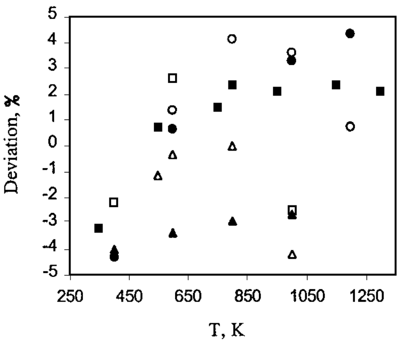

Fig. 1. Average percentage deviation, $(\rho_{\text{calc}}/\rho_{\text{exp}} - 1) \times 100$, of the density of molten alloys of K–Cs (■), Na–K (●), and Na–K–Cs (▲) with the experimental values [30, 31]. The corresponding open symbols are from the previous work [25].

Table I. Density of Alkali Metals

T (K)	P (bar)	ρ_{calc} $(\text{mol} \cdot \text{L}^{-1})$	ρ_{exp} $(\text{mol} \cdot \text{L}^{-1})$	Dev. (%)
		0.1 K + 0.8 Cs		
350	2.532×10^{-9}	13.67	14.17	−3.53
550	1.385×10^{-3}	13.24	13.29	−0.39
750	9.224×10^{-2}	12.41	12.40	0.05
950	1.021	11.55	11.50	0.43
1150	4.809	10.62	10.57	0.47
1300	11.00	9.82	9.85	−0.34
		0.2 K + 0.8 Cs		
350	2.403×10^{-9}	14.15	14.74	−4.00
550	1.253×10^{-3}	13.79	13.84	−0.36
750	8.495×10^{-2}	12.95	12.92	0.18
950	0.9559	12.07	11.98	0.71
1150	4.579	11.12	11.03	0.86
1300	10.59	10.31	10.33	−0.16

Table I. *(Continued)*

T (K)	P (bar)	ρ_{calc} (mol · L^{-1})	ρ_{exp} (mol · L^{-1})	Dev. (%)
		0.3 K + 0.7 Cs		
350	2.274×10^{-9}	14.73	15.33	−3.91
550	1.122×10^{-3}	14.38	14.39	−0.09
750	7.765×10^{-2}	13.52	13.45	0.53
950	0.8909	12.62	12.49	1.03
1150	4.350	11.66	11.52	1.21
1300	10.18	10.84	10.80	0.41
		0.4 K + 0.6 CS		
350	2.145×10^{-9}	15.34	15.85	−3.22
550	9.899×10^{-4}	15.01	14.91	0.70
750	7.036×10^{-2}	14.14	13.94	1.39
950	0.8259	13.22	12.97	1.91
1150	4.121	12.24	11.98	2.11
1300	9.768	11.40	11.24	1.47
		0.505 K + 0.495 Cs		
350	2.009×10^{-9}	16.06	16.37	−1.89
550	8.515×10^{-4}	15.73	15.39	2.21
750	6.270×10^{-2}	14.84	14.43	2.83
950	0.7576	13.89	13.42	3.47
1150	3.880	12.89	12.43	3.68
1300	9.336	12.04	11.68	3.09
		0.6 K + 0.4 Cs		
350	1.886×10^{-9}	16.86	17.10	−1.40
550	7.263×10^{-4}	16.42	16.09	2.06
750	5.576×10^{-2}	15.52	15.09	2.85
950	0.6958	14.54	14.06	3.46
1150	3.662	13.52	13.02	3.79
1300	8.946	12.66	12.23	3.54
		0.7 K + 0.3 Cs		
350	1.757×10^{-9}	17.51	18.10	−3.26
550	5.945×10^{-4}	17.22	17.06	0.93
750	4.847×10^{-2}	16.29	15.99	1.91
950	0.6308	15.14	14.62	3.56
1150	3.433	13.89	13.52	2.74
1300	8.457	13.19	12.97	2.46

Table I. *(Continued)*

T (K)	P (bar)	ρ_{calc} (mol · L^{-1})	ρ_{exp} (mol · L^{-1})	Dev. (%)
		0.8 K + 0.2 Cs		
350	1.628×10^{-9}	18.24	18.98	−3.90
550	4.628×10^{-4}	18.08	17.94	0.78
750	4.117×10^{-2}	17.14	16.83	1.80
950	0.5658	16.10	15.71	2.46
1150	3.204	15.02	14.59	2.96
1300	8.125	14.13	13.69	3.21
		0.9 K + 0.1 Cs		
350	1.499×10^{-9}	19.30	19.95	−3.25
550	3.310×10^{-4}	19.02	18.87	0.79
750	3.388×10^{-2}	18.06	17.72	1.90
950	0.5007	16.98	16.54	2.63
1150	2.974	15.87	15.35	3.40
1300	7.715	14.96	14.44	3.58
		0.1 Na + 0.8 K		
400	3.498×10^{-7}	21.16	21.98	−3.69
600	1.314×10^{-3}	20.95	20.73	1.06
800	7.465×10^{-2}	19.86	19.50	1.85
1000	0.8167	18.70	18.19	2.80
1200	4.093	17.50	16.88	3.67
		0.2 Na + 0.8 K		
400	2.700×10^{-7}	22.27	23.24	−4.20
600	1.111×10^{-3}	22.14	21.96	0.82
800	6.632×10^{-2}	21.04	20.65	1.89
1000	0.7565	19.84	19.31	2.74
1200	3.925	18.60	17.95	3.62
		0.3 Na + 0.7 K		
400	2.055×10^{-7}	23.49	24.63	−4.63
600	9.077×10^{-4}	23.44	23.26	0.77
800	5.700×10^{-2}	22.34	21.89	2.01
1000	0.6747	21.09	20.49	2.93
1200	3.605	19.81	19.08	3.82
		0.402 Na + 0.598 K		
400	1.561×10^{-7}	24.87	26.11	−4.75
600	7.358×10^{-4}	24.91	24.67	0.97
800	4.842×10^{-2}	23.79	23.20	2.54
1000	0.5950	22.50	21.73	3.54
1200	3.277	21.18	20.26	4.49

Table I. *(Continued)*

T (K)	P (bar)	ρ_{calc} $(\text{mol} \cdot \text{L}^{-1})$	ρ_{exp} $(\text{mol} \cdot \text{L}^{-1})$	Dev. (%)
		0.5 Na + 0.5 K		
400	1.184×10^{-7}	26.65	27.80	−4.13
600	5.897×10^{-4}	26.48	26.32	0.61
800	4.069×10^{-2}	25.35	24.74	2.46
1000	0.5201	24.00	23.22	3.36
1200	2.953	22.63	21.64	4.52
		0.6 Na + 0.4 K		
400	8.794×10^{-8}	28.65	29.69	−3.81
600	4.634×10^{-4}	28.26	28.10	0.57
800	3.377×10^{-2}	27.12	26.46	2.45
1000	0.4519	25.71	24.83	3.54
1200	2.654	24.27	23.20	4.69
		0.681 Na + 0.319 K		
400	6.708×10^{-8}	29.89	31.46	−4.99
600	3.739×10^{-4}	29.87	29.79	0.27
800	2.885×10^{-2}	28.71	28.08	2.24
1000	0.4045	27.25	26.38	3.29
1200	2.450	25.77	24.67	4.45
		0.8 Na + 0.2 K		
400	4.118×10^{-8}	32.57	34.03	−4.26
600	2.624×10^{-4}	32.56	32.39	0.52
800	2.297×10^{-2}	31.38	30.60	2.55
1000	0.3523	29.82	28.76	3.68
1200	2.252	28.25	26.93	4.90
		0.9 Na + 0.1 K		
400	2.225×10^{-8}	35.32	36.91	−4.31
600	1.854×10^{-4}	35.20	35.04	0.45
800	1.958×10^{-2}	33.97	33.09	2.66
1000	0.3327	32.32	31.19	3.82
1200	2.238	30.65	29.18	5.00
		0.1005 Na + 0.4749 K + 0.4246 CS		
400	1.712×10^{-6}	17.71	18.46	−4.06
600	2.843×10^{-3}	16.81	17.39	−3.35
800	0.1162	15.85	16.33	−2.90
1000	1.087	14.86	15.26	−2.64

Na, K, and Cs are 0.383, 0.381, and 0.385, respectively. The interaction parameters of $(B_2)_{ij}$, α_{ij}, and b_{ij} are calculated with Eqs. (5)–(12). The K–Cs mixtures are ideal [28], and the vapor pressures are calculated using Raoult's law. The activity coefficient data of Kagan et al. [29] were used to calculate the vapor pressure of K–Na mixtures. Because of the lack of experimental vapor pressure data for the K–Na–Cs mixture, we have used the simple Raoult's law to calculate the vapor pressure of the mixture. The liquid densities of K–Cs and K–Na mixtures over the whole range of concentration and a ternary eutectic mixture of Na–K–Cs were calculated from the freezing point up to several hundred degrees above the boiling point and are compared with experimental values of Skovordko [30] and Tepper et al. [31], respectively, in Table I. The calculated values have been compared with the previous work in Fig. 1. The agreement with experiment is much better than that of the previous work [25].

5. CONCLUSIONS

This work demonstrates that the entire p–v–T surface of molten alkali metal alloys can be constructed with reasonable accuracy from just two scaling constants, γ_b and ρ_b, without invoking "mixing rules." The equation of state applied to mixtures maintains almost the same accuracy as the energy and size parameters of the components are varied. This feature distinguishes the theory from most existing theories, for which the accuracy is generally good only when the component parameters are not very different. Even for the steepest liquid branch, the agreement of the calculated results with experiment [30, 31] is within 5%.

Although the interatomic potentials of alkali metals are inherently different in liquid and vapor phases, Eq. (8) with the Lennard–Jones (12–6) potential used to calculate $\alpha(T)$ and $b(T)$ still produces relatively accurate results. The reason is that α and b depend only on the repulsive branch of the interatomic potential and hence are relatively insensitive to the detailed shape of the potential. The free parameter of the equation of state, on the other hand, compensates for inaccuracies associated with the temperature-dependent parameters.

The cohesive energy density can be represented by both the heat of vaporization and the surface tension. Comparison of our results with previous work [25] shows that a choice of the surface tension as a scaling constant is better than the heat of vaporization, so that the results cover a much wider range of temperatures and are in better agreement with experiment [30, 31]. In summary, statistical mechanics now allows the equation of state of alkali metals and their alloys to be predicted from simple measurements at ordinary temperatures and pressures.

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