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A Perturbed Hard-Sphere Equation of State for Alkali Metal Alloys

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A perturbed hard-sphere equation of state for liquid alkali metals has been employed to calculate the liquid density of alkali metal alloys over a wide range of temperature. Two temperature-dependent parameters appear in the equation of state, which are universal functions of the reduced temperature, i.e., two scale parameters are sufficient to calculate the temperature-dependent parameters, and hence, to predict the equation of state. In this article, calculated results of the liquid density of binary molten alloys of Na–K and K–Cs over the whole range of concentration at temperatures from the freezing point up to several hundred kelvin above the boiling point reproduce accurately the experimental PVT data points.

KEY WORDS: alkali metals; alloys; density; equation of state; statistical mechanics.

1. INTRODUCTION

Alkali metals and their alloys have a unique combination of physicochemical properties, such as extremely high electrical and thermal conductivities, low vapor pressures, low densities and viscosities, low melting temperatures and work functions, wide temperature ranges of the liquid state, high heats of evaporation, etc. Therefore, they are widely used in modern science and technology, for example, in nuclear energetics, emission electronics, new power-intensive chemical current sources, and medicine. During recent years considerable interest has been shown in the use of liquid metals, particularly sodium and sodium–potassium alloys [1], as heat transfer

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media in the field of nuclear-power generation. This interest was stimulated by the need to remove large quantities of heat from nuclear-power reactors at moderate coolant velocities and temperature drops.

Equation-of-state theory gives us very useful information in investigating the properties of fluids and fluid mixtures. It contains essential information about a substance, and any equilibrium property can be obtained from the fundamental equations of state by applying the appropriate thermodynamic relations. Most modern molecular thermodynamic theories of liquid and liquid mixtures are based on the prediction of the properties of hard-sphere systems [2,3]. The hard-sphere fluid is taken into account as a reference system, and the influence of attractions and the softness of repulsions are considered as perturbations in statistical-mechanical perturbation theories of fluids [4,5].

Previously Maftoon Azad et al. [6] have developed a perturbed hard-sphere equation of state to calculate PVT properties of alkali metals over a wide range of temperatures and pressures. It is the purpose of this work to employ the previous equation of state to predict the density of molten alkali metal alloys.

2. Theory

2.1. Equation of State for Pure Fluids

In the perturbed hard-sphere equation of state, the total pressure consists of contributions from hard-sphere repulsion and the attractive van der Waals forces between spheres;

$$P = P_{\text{hard-sphere}} + P_{\text{vdWattraction}} \tag{1}$$

which can be written in the following form [7]:

$$\frac{P}{\rho kT} = 1 + b\rho g(d^{+}) - \frac{a\rho}{kT} \tag{2}$$

where P is the pressure, $\rho = N/V$ is the number density, kT is the thermal energy per molecule, $g(d^{+})$ is the pair radial distribution function of hard spheres at contact, a reflects the strength of attractive forces between spheres, and b is the van der Waals covolume. The Carnahan and Starling expression for $g(d^{+})$ [7] is remarkably accurate;

$$g(d^{+}) = \frac{1 - \eta/2}{(1 - \eta)^3} \tag{3}$$

where η is the packing fraction defined as

$$\eta = \frac{1}{4} b\rho \tag{4}$$

Recent works by Song and Mason [8] and Ihm et al. [9] on the statistical-mechanical perturbation theories of fluids led to explicit analytical expressions for the calculation of the van der Waals covolume and the strength of intermolecular attractive forces in terms of the potential energy function; however, the potential energy function is seldom accurately known. Song and Mason [8] showed that the temperature-dependent parameters, a and b, are rather insensitive to the shape of the potential energy function, $u(r)$, and of course not to its magnitude, so that they appear as almost universal functions of temperature in terms of suitable reduced units. The expressions for a and b, as defined in our previous study [6] are written as

$$a(T) = \frac{2\pi}{3} V_{\mathrm{b}} T_{\mathrm{b}} k F_{\mathrm{a}} \left(\frac{T}{T_{\mathrm{b}}}\right) \tag{5}$$

and

$$b(T) = \frac{2\pi}{3} V_{\mathrm{b}} F_{\mathrm{b}} \left(\frac{T}{T_{\mathrm{b}}}\right) \tag{6}$$

where V_{b} is the volume at the normal boiling point, T_{b} is the normal boiling point temperature, and F_{a} and F_{b} are universal functions of the reduced temperature (T/T_b) and can be correlated according to [6]

$$F_{\mathrm{a}} \left(\frac{T}{T_{\mathrm{b}}}\right) = a_1 \exp\left(-a_2 \frac{T}{T_{\mathrm{b}}}\right) + a_3 \exp\left[-a_4 \left(\frac{T}{T_{\mathrm{b}}}\right)^{3/2}\right] \tag{7}$$

and

$$F_{\mathrm{b}} \left(\frac{T}{T_{\mathrm{b}}}\right) = b_1 \exp\left(-b_2 \frac{T}{T_{\mathrm{b}}}\right) + b_3 \exp\left[-b_4 \left(\frac{T}{T_{\mathrm{b}}}\right)^{3/2}\right] \tag{8}$$

where the coefficients a_i and b_i are determined empirically. These coefficients are determined by fitting to P–V–T data points of alkali metals [6] and have been determined as follows:

$a_1 = 1.173309$ $a_2 = -0.613249$

$a_3 = 0.670328$ $a_4 = -0.108354$

$b_1 = 0.592740$ $b_2 = 0.593157$

$b_3 = 0.307474$ $b_4 = -0.264451$

2.2. Equation of State for Fluid Mixtures

To extend the proposed model to fluid mixtures, the equation can be written as

$$\frac{P}{\rho kT}=1+\rho\sum_{i}^{m}\sum_{j}^{m}x_i x_j b_{ij} g_{ij}-\frac{\rho}{T}\sum_{i}^{m}\sum_{j}^{m}x_i x_j a_{ij} \tag{9}$$

where x_i and x_j are mole fractions of components i and j, respectively, and the summations run over all the components; $g_{ij}(d_{ij}^{+})$ is the pair radial distribution function of hard-sphere mixtures, which takes the form of the Boublik–Mansoori–Carnahan–Starling(BMCS) equation [10]:

$$g_{ij}(\eta,\xi_{ij})=\frac{1}{1-\eta}+\frac{3}{2}\frac{\xi_{ij}}{(1-\eta)^2}+\frac{1}{2}\frac{\xi_{ij}^2}{(1-\eta)^3} \tag{10}$$

with

$$\eta=\frac{\rho}{4}\sum_{i}^{m}x_i b_i \tag{11}$$

$$\xi_{ij}=\left(\frac{b_i b_j}{b_{ij}}\right)^{\frac{1}{3}}\frac{\rho}{4}\sum_{k}^{m}x_k b_k^{2/3} \tag{12}$$

The hard-sphere diameters are additive; therefore, $b_{ij}(T)$ can be expressed as

$$b_{ij}=\frac{2\pi}{3}d_{ij}^3(T)=\frac{1}{8}(b_i^{1/3}+b_j^{1/3})^3 \tag{13}$$

And the temperature-dependent parameter $a_{ij}(T)$, which describes the attractive forces between species i and j, is written as

$$a_{ij}(T)=\frac{2\pi}{3}(V_{\mathrm{b}})_{ij}(T_{\mathrm{b}})_{ij}kF_{ij}(T/T_{\mathrm{b}}) \tag{14}$$

Table I. Constants Used for Alkali Metals [11]

Metal	T_{b}(K)	V_{b}($\mathrm{L\cdot mol^{-1}}$)
Na	1156.3	0.031016
K	1030.4	0.058
Cs	942.3	0.0904151

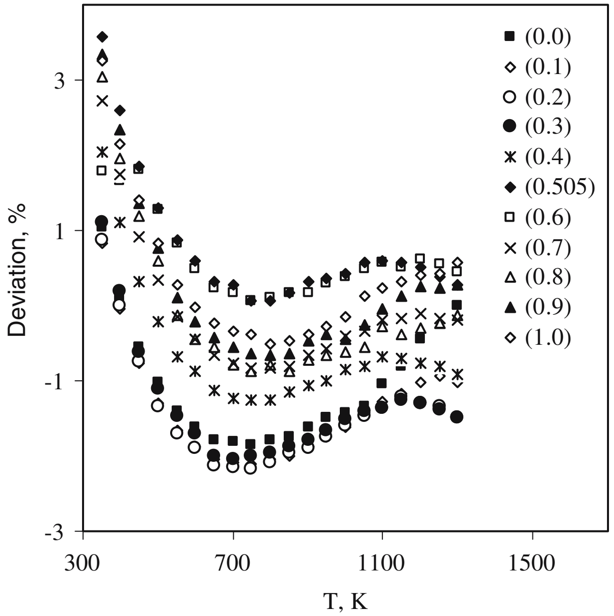

Fig. 1. Density of $xK+(1-x)$Cs alloys as a function of temperature. Numbers in parentheses show x values.

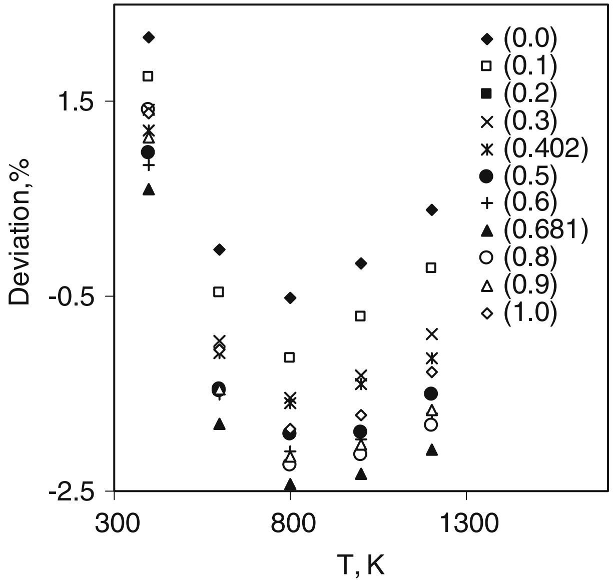

Fig. 2. Same as Fig. 1 for xNa$+(1-x)$ K alloy.

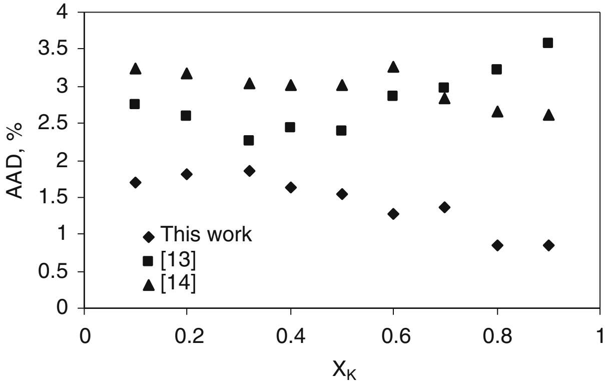

Fig. 3. Average absolute deviations for the predicted density of Na–K alloys compared with Refs. [13, 14].

for which the following combination rules are applied for $(T_b)_{ij}$ and $(V_b)_{ij}$:

$$(T_{\mathrm{b}})_{ij} = \sqrt{(T_{\mathrm{b}})_{ii}(T_{\mathrm{b}})_{jj}} \tag{15}$$

$$\sqrt[3]{(V_{\mathrm{b}})_{ij}} = \frac{\sqrt[3]{(V_{\mathrm{b}})_{ii}} + \sqrt[3]{(V_{\mathrm{b}})_{jj}}}{2} \tag{16}$$

and

$$F_{ij}\left[T/(T_{\mathrm{b}})_{ij}\right] = \left\{F_{\mathrm{a}}\left[T/(T_{\mathrm{b}})_{ii}\right]F_{\mathrm{a}}\left[T/(T_{\mathrm{b}})_{jj}\right]\right\}^{1/2} \tag{17}$$

3. RESULTS AND DISCUSSION

As mentioned in the previous section, the temperature-dependent parameters of the equation of state, a and b, can be calculated with a knowledge of the full potential energy curve, or more simply, using the empirical formulas, Eqs. (5) and (6). The constants in Eqs. (7) and (8) for F_{a} and F_{b} are fitted to the P–V–T data points of all alkali metals [6]. The only scaling parameters required for this equation of state are V_{b} and T_{b} which are easily available, and no other adjustable parameter is required. T_{b} and V_b values are taken from Ref. [11] and are listed in Table I.

We have calculated the densities of alkali metal alloys over the whole range of concentrations. The experimental densities are taken from Ref. [12]. The deviations of our predicted values from experimental densities

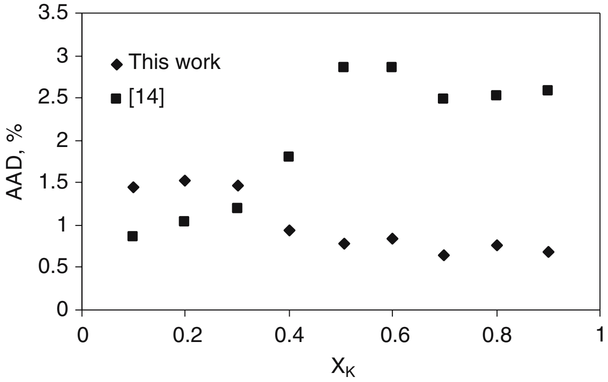

Fig. 4. Average absolute deviations for the predicted density of K–Cs alloys compared with Ref. [14].

are shown in Figs. 1 and 2. Analysis of the results shows that we can obtain very good results with a maximum deviation of 4% and an average absolute deviation of 1.08%. We have also compared the predicted results from the present work for K–Cs and Na–K mixtures with those of previous studies [13, 14] in Figs. 3 and 4, respectively. The results show that the presented equation of state is more accurate with respect to the previous studies [13, 14].

4. CONCLUSIONS

Our results in this work show that the equation of state for liquid metals and their mixtures can be obtained with a knowledge of just two simple scaling constants, T_b and V_b. There is no need to know the full potential energy function. This is somehow due to the fact that the temperature-dependent parameters, a and b, are insensitive to the details of the potential energy function and obey a simple law of corresponding states, as is indicated in our previous studies [6, 14]. Here, we showed that by reducing a and b with normal boiling point constants, which are readily available, we can produce relatively accurate results.

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