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Temperature-Dependent Dispersion Coefficients of Alkali Metals Using Equation of State

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Abstract

In this study, a temperature-dependent of the dispersion coefficients is calculated from equation of state. The Lennard-Jones LJ (12-6-3) effective pair potential function and simple thermodynamic argument with the input *PVT* data of liquid metals are used to calculate the dispersion coefficients. The dispersion coefficients (C_3, C_6, C_{12}) are found to be a linear function of $1/T^{1+\alpha}$, where T is the temperature and α is a constant and has different values for different dispersion coefficients. The law of corresponding states based on the reduced dispersion coefficients and reduced temperature is used to verify the validity of a LJ (12-6-3) potential function in describing the dispersion coefficients. By applying the dispersion coefficients of alkali metals and potential function plots, the values of molecular parameters (σ , ϵ , and r_m) have been obtained. The LJ (12-6-3) potential function conclusively predicts the best dispersion coefficients of the three alkali metals (K, Rb, and Cs).

Keywords: Dispersion Coefficient, Equation of State, Alkali Metals

1. Introduction

Alkali metals are useful for their marked thermodynamic properties such as high heats of vaporization and large liquid ranges, which make them good heat transfer fluids in reactors operating at high temperature, at high energy rate, and nuclear power reactors [1,2]. These applications raise the problem of accurately knowing the thermodynamic properties. An important application of equations of state is to predict the thermodynamic properties and

interatomic interaction such as dispersion coefficients of pure substances and fluid mixtures [3,4]. The accuracy of predicted thermodynamic properties by equation of state depends on the accuracy of pair potential function describing the interatomic interaction of these metals.

For some dense fluids, Parsafar et al. [5,6] employed an effective pair potential of the Lennard-Jones (LJ) (12-6) type to obtain an equation of state that that isotherms plotted as $(Z-1)V^2$ versus ρ^2 tend to be linear, where Z is the compressibility factor, ρ is the molar density, and V the molar volume. In cases

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where it was applied to simple atomic and molecular liquids in which their intermolecular interactions originate from dispersion forces, the intercept of linear isotherm to conform to the second virial coefficient (B_2). Ghatee and Bahadori [7] proposed the softer LJ(6-3) potential to obtain an accurate equation of state for liquid cesium and other liquid metals. The slope (B) of this linear isotherm mimics the corresponding theoretical B_2 value, although its absolute value is smaller (by up to 4 orders of magnitude at the melting temperature and by a factor of 1/2 at the critical temperature). Interestingly, both B_2 and B span in the negative region [8], so much so that the Boyle temperature (T_B) is never reached. The LJ (8.5-4) potential function also leads to a promising linear isotherm over the entire liquid range. Again, the slope of this isotherm (B') conforms to the theoretical B_2 value [9].

In this paper, we study the dispersion coefficients (C_3, C_6, C_{12}) of three alkali metals (K, Rb, and Cs). The dispersion coefficients are predicted by the application of only experimental liquid PVT data [10, 11] in a wide temperature and pressure range. Equation of state by using Lennard-Jones (12-6-3) potential function is derived [12]. Knowledge of the temperature dependence of the dispersion coefficients would greatly increase its predictive power with minimal input data. This is especially important for geophysical applications, where knowledge of high-pressure and high-temperature behavior is often necessary but direct measurement is difficult.

2. The Method

a) Potential Function

For a large number of atomic and molecular fluids, LJ (12-6) potential function accounts for the pairwise interaction approximation between the fluid molecules undergoing dispersive interaction as the major interaction [5]. Liquid alkali metals have been treated thermodynamically by methods of dense normal fluids [5], in which case the structure of liquid is determined essentially by the repulsive side of the potential function.

Since the single valence electrons of the two colliding alkali metal atoms overlap to form a weak chemical bond, it causes the repulsion potential becomes softer than those of normal fluids. On the other hand, alkali metal atoms in liquid state are readily polarized such that the potential function at long range is contributed by more attraction than those of normal fluids [7]. In particular the potential of a light alkali metal has a narrow and deep (hard repulsion) potential well, and a heavy alkali metal has a wide and shallow (soft repulsion) potential well. From analysis of the neutron scattering of liquid cesium as a function of temperature and pressure of the liquid cesium, the values of $m=6$ and $n=3$ have been determined, and thus the pair potential function $u(r_{ij}) = A\varepsilon [(\sigma/r_{ij})^6 - (\sigma/r_{ij})^3]$ has been proposed to account for the interatomic interaction and to predict the thermodynamic properties of cesium fluid more accurately [7]. Parsafar and Mason proposed a more general effective near-neighbor pair potential, such that the total configurational energy of an N particle system is given by [12]:

$$u(r) = \left(\frac{C_6}{r^6} + \frac{C_3}{r^3} + \frac{C_{12}}{r^{12}} \right) \quad (1)$$

$$u(r) = \mathring{a} \left(\frac{C_6^*}{x^6} + \frac{C_3^*}{x^3} + \frac{C_{12}^*}{x^{12}} \right)$$

Here, the coefficient C_6 describes the dipole-dipole interaction, C_8 the dipole-quadrupole interaction, and C_{12} the quadrupole-octupole as well as the dipole-hexadecapole interactions, and $x = r/r_m$, in which r is the interatomic distance. The potential function of Eq. (1) obeys boundary conditions of a potential function such that r_m is the position of potential minimum, \mathring{a} is the potential well depth, and $u(r) = 0$ at $r = \sigma$, that σ is the hard sphere diameter. The second potential function in Eq. 1 is reduced form that $C_i(T) = \mathring{a} C_i^*(T) r_m^i$.

b) Equation of State and Linear Isotherm

The LJ(12-6-3) potential function in Eq. (1) is applied to evaluate the interaction potential energy of the liquid state, assuming that the liquid obeys our recent model [5,7]

having the following details. The liquid lattices K, Rb, and Cs close to their freezing points have body-centered cubic (bcc). Therefore in this structure alkali metals have 8 nearest neighbors. In this model, to calculate the total interaction potential energy, the complete pairwise additivity of the interaction potential is assumed. Therefore, the total potential energy of an N -particle system $U(r_1, \dots, r_N) = \sum_{i>j=1}^N u(r_i, r_j)$, where the pair potential $u(r_i, r_j)$ is often assumed to depend only on the distance $r_{ij} = |r_i - r_j|$ between the i th and j th pair of particles located at positions r_i and r_j , respectively. Furthermore, it is assumed that any particle interacts only with its nearest adjacent particles in pairs, like a pair of particles 1 and 2 with pair potential $u(r_{12})$, and thus the potential energy

$$U(r_1, \dots, r_N) = \frac{1}{2} N u(r_{12}). \quad (2)$$

In the next step of modeling, the accurate mechanical pressure, P , of the liquid system is estimated by the solution of the thermodynamic equation of state:

$$P = T \left(\frac{\partial P}{\partial T} \right)_{\tilde{n}} - P_{\text{int}} \quad (3)$$

where T is the absolute temperature, $\tilde{n} = 1/V$ is the molar density, and V is the molar volume. The internal pressure is expressed as,

$$P_{\text{int}} = \left(\frac{\partial(U + E_K)}{\partial V} \right)_T \quad (4)$$

where E_K is the kinetic energy of N -particle system. Since $(\partial E_K / \partial V)_T = 0$ then,

$$P = T \left(\frac{\partial P}{\partial T} \right)_{\tilde{n}} - \left(\frac{\partial U}{\partial V} \right)_T \quad (5)$$

By substituting Eq. (1) into Eq. (2) and combining Eq. (2) with Eq. (5), we present the equation of state as the following isotherm:

$$(Z-1)V^2 = F_6(T) + \frac{F_3(T)}{\rho} + \frac{F_{12}(T)}{\rho^2} + a_2 \quad (6)$$

$$F_6(T) = \frac{-N C_6}{K^6 R T}, F_3(T) = \frac{-N C_3}{2K^3 R T}, F_{12}(T) = \frac{-2N C_{12}}{K^{12} R T}$$

where R is the gas constant, Z is the compression factor, N is Avogadro's number, and K is the lattice constant. This model requires knowledge of the coordination number of a given particle in an N -particle liquid system. This involves a lattice constant that depends on the assumed structure for the system. The (lattice) structure of liquid alkali metals is approximated by a body-centered cubic [$K = \sqrt{3} / (4N)^{1/3} = 1.29 \times 10^{-8}$]. It should be noticed that K is the proportionality constant between the equilibrium intermolecular distance and the molar volume,

e.g. $r = K V^{1/3}$, of the corresponding system.

Where, $a_2 = \frac{1}{R \rho^3} \left[\left(\frac{\partial P}{\partial T} \right)_v - R \rho \right]$ is the

contribution from the nonideal thermal pressure and it is calculated from the experimental PVT data [10,11] of the system under consideration. The potential parameters, C_3, C_6 , and C_{12} , are determined on fitting to experimental data. This procedure is applied to characterize the LJ(12-6-3) potential function for three alkali metals (K, Rb, Cs). This method also yields additional information about the validity of molecular potential parameters (\tilde{a} , $\tilde{\sigma}$, and r_m) of systems whose major interatomic interaction is the dispersion type interaction, e.g. C_3, C_6 , and C_{12} .

3. Results and Discussion

a) Potential Function and Equation of State

Parsafar and Mason [5] assumed effective potential of the LJ(12-6) form with temperature-independent parameters and obtained equation of state $(Z-1)V^2 = a + b/\rho^2$ form, where a and b are related to the attractive and repulsive terms of the effective potential, respectively. This equation of state has been used to explain some experimentally well-known regularity and also to predict some that were previously

unknown and it only depends on ρ^2 . Ghatee and Bahadori [7] proposed that an effective potential of the LJ(6,3) form be used with temperature independent coefficients. In particular, they [7] suggested that the LJ(6-3) potential would “soften” the core repulsion and that the r^{-3} term would help account for the longer-ranged, slowly decaying interaction found for liquid cesium. They obtained the equation of state $(Z-1)V^2 = c + d/\rho$, where c and d are related to the attractive and repulsive parts of the effective potential, respectively. Ghatee and Bahadori [7] showed that it gives a good description of the equation of state for cesium over its entire liquid range and it consists of only $1/\rho$ term.

To find dispersion coefficients for alkali metals (K, Rb, Cs), we assumed the effective pair potential Eq. 1 that is of an Extended Lennard-Jones (12-6-3) form with temperature-dependent coefficients [12]. The LJ(12-6-3) pair potential function used in this study consists of long range attraction terms in the form of multipolar interaction terms. Then equation of state (Eq. 6) is obtained that consists of both the ρ^2 dependence and the $1/\rho$. Physically, terms proportional to r^{-6} and r^{-2} can be justified in an effective potential because a dispersion interaction, together with a term representing the repulsive cores, is expected to be present for molecules of all types. The r^{-3} term, which gives the $1/\rho$ contribution in Eq. 6, is harder to rationalize because, apart from molecules with permanent dipoles, we would not expect a term proportional to r^{-3} in the true pair potential. However, here, we are considering a model where the total configurational energy is represented by effective near-neighbor interactions [12]. Thus, one can simply view the r^{-3} term as a “stand in” for all contributions to the energy that cannot be represented by the LJ(12-6) interaction.

The dispersion coefficients (C_3, C_6, C_{12}) of the LJ(12-6-3) potential function are obtained by fitting the isotherm (6) to the most recent experimental PVT data of liquid alkali metals at high pressure [10,11]. Dispersion coefficients are temperature dependent. It turns out that the model potential function becomes

temperature dependent. Therefore the method is accurate in the thermodynamic sense but also it provides means for the accurate determination of an effective interaction potential function. For alkali metals (K, Rb, Cs), fitting is made at temperature range 500 K to 1600 K and in the pressure range 10 to 100 bar.

Since the temperature dependence of the $C_i(T)$ coefficients in Eq. 1 is not known, knowledge of the temperature dependence of the three parameters in Eq. 1 is valuable and would greatly increase its predictive power with minimal input data. This is especially important for geophysical applications, where knowledge of high-pressure and high-temperature behaviors is often necessary but direct measurement is difficult. It is important to compare dispersion coefficients of three alkali metals (K, Rb, Cs) with together. These comparisons are shown in figures 1a, 1b, and 1c for C_3, C_6 , and C_{12} , respectively. Notice that the values of dispersion coefficients (C_3, C_6 , and C_{12}) vary smoothly with temperature and the C_6 and C_{12} increases with temperature although C_3 decreases as temperature is increased. C_3, C_6 coefficients are related to the attractive part of the effective potential and C_{12} to the repulsive part of effective potential. The values of dispersion coefficients C_3, C_6 of potassium alkali metal are the smallest. Therefore the potential function of potassium has a smaller attraction than cesium and rubidium potential functions at long range and it has a larger repulsion. Thus, the smaller size of an alkali metal atom has the harder electronic cloud.

The linearity of C_3, C_6 , and C_{12} versus $1/T^{(1+\alpha)}$ [13] with $\alpha = -0.7, -5.31$, and -4.13 reported for three alkali metals (K, Rb, Cs). One can conclude that the linearity holds well, with $R^2 \geq 0.9958$. Figure 2 shows the linearity of C_3 versus $1/T^{(1+\alpha)}$ with $\alpha = -0.7$.

By applying calculated dispersion coefficients and construction plot of potential function at different temperatures, the values of molecular parameters ($\hat{a}, \hat{\sigma}, r_m$) have been obtained. The r_m , increases almost linearly with temperature. The values of ε/k_B are

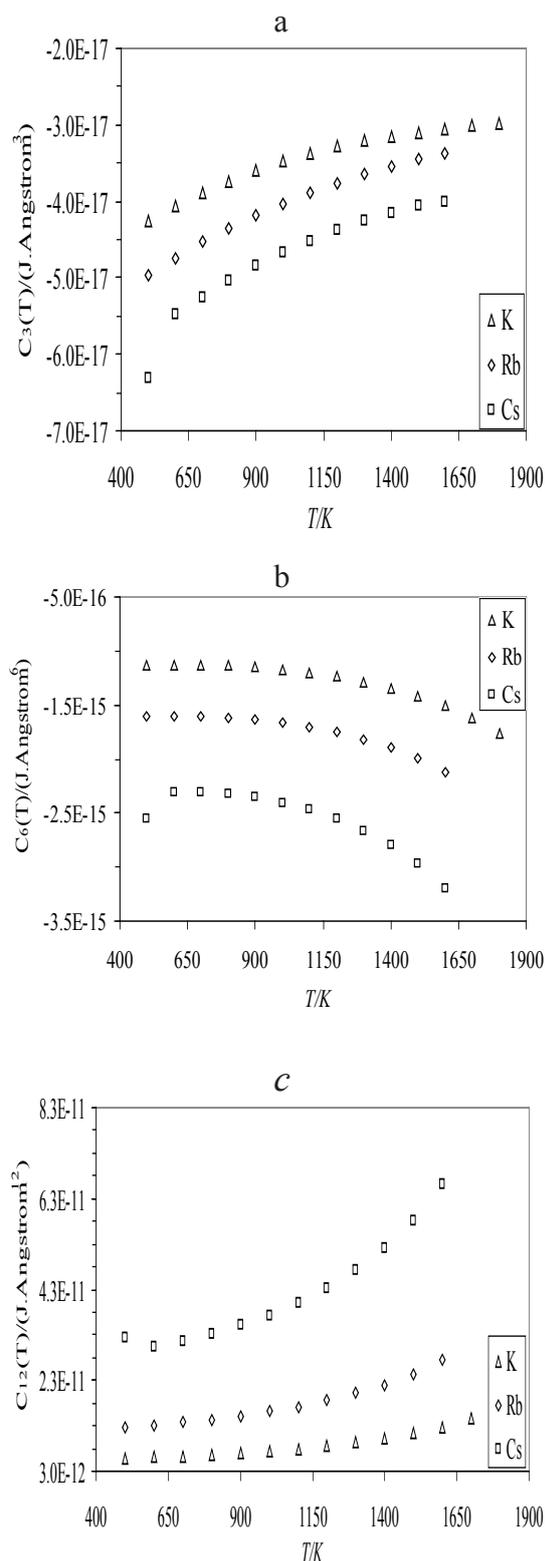


Fig.1. Plots of a) dispersion coefficient C_3 , b) dispersion coefficient C_6 , c) dispersion coefficient C_{12} vs. temperature for K, Rb, Cs, respectively.

calculated; these values smoothly decrease as temperature increase. The value of ε in our model is actually the interaction energy of an alkali metal atom with all its nearest

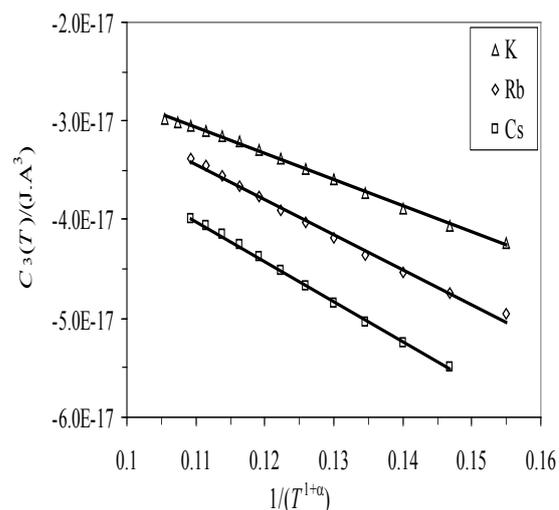


Fig. 2. The linearity of C_3 versus $1/T^{(1+\alpha)}$ with $\alpha = -0.7$ for three alkali metals (K, Rb, Cs) in the temperature range 500 K- 1600 K.

neighboring atoms. Indeed, we have to include the values of coordination number to have a meaningful potential well-depth. To achieve this we have used the experimental coordination number reported in Refs. 14-16. Then the coordination number at a particular T could be obtained by a smooth interpolation. Now, by these coordination numbers, it is seen that ε/k_B smoothly decreases with temperature. The values of $\overset{\circ}{a}$, $\overset{\circ}{\sigma}$, and r_m for K, Rb, and Cs at temperature 500 K are summarized in Table 1.

Table 1: Molecular parameters ($\overset{\circ}{a}$, $\overset{\circ}{\sigma}$, r_m) for K, Rb, and Cs.

	K	Rb	Cs
$\overset{\circ}{\sigma}$ (Å)	4.07	4.40	4.62
r_m (Å)	4.88	5.20	5.26
ε/k_B (K)	974.89	901.57	832.16

b) Law of corresponding states

It is valuable to present the dispersion coefficients as a universal function in the context of the law of corresponding states for validation and prediction dispersion coefficients. Calculated molecular parameters $\overset{\circ}{a}$ and r_m (reported in Table 1) based on LJ (12-6-3) potential, can be used to determine the

reduced dispersion coefficients, as a function of reduced temperature, $T^* = T(\tilde{a}/k_B)$. The correlations of C_3^* , C_6^* , and C_{12}^* as functions of T^* for various metals are shown in figures 3a, 3b, and 3c, respectively. The correlation

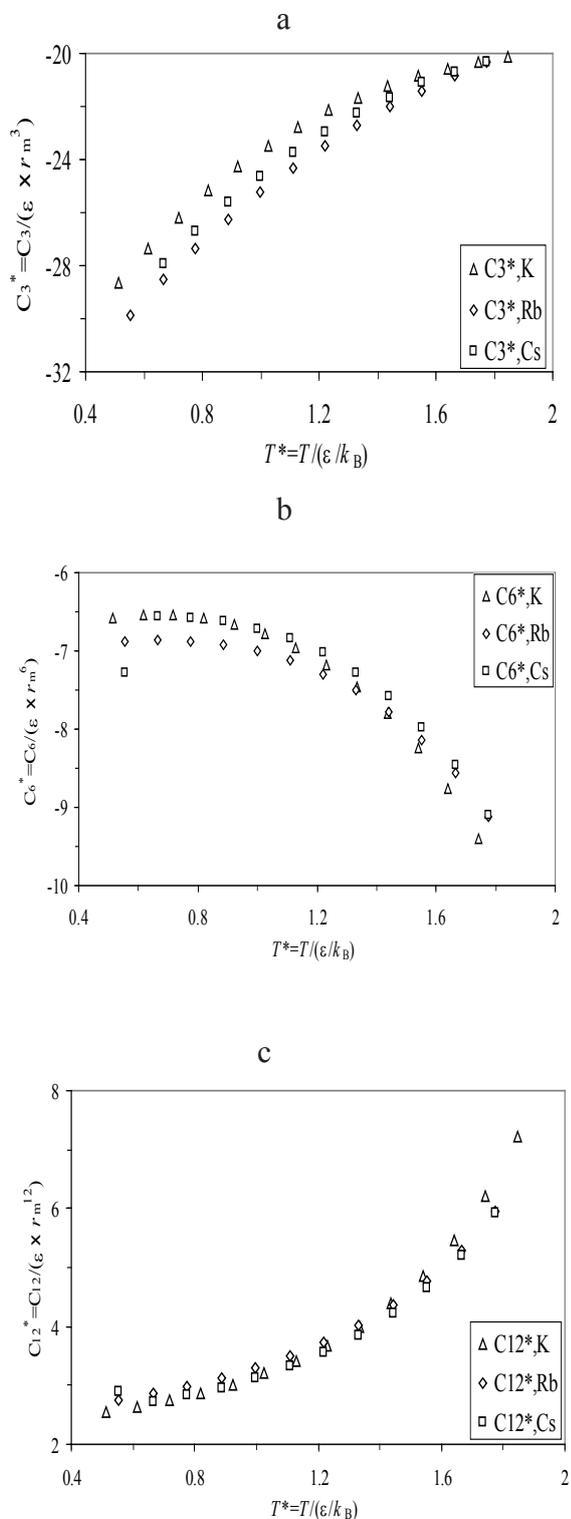


Fig. 3. Plots of a) reduced dispersion coefficient C_3^* , b) reduced dispersion coefficient C_6^* , c) reduced dispersion coefficient C_{12}^* , vs. reduced temperature T^* for K, Rb, Cs metals.

between three alkali metals in figures 3 is strong and can be attributed to relatively high accuracy the LJ (12-6-3) potential function.

4. Conclusions

Accurate equation of state for potassium, rubidium, and cesium metals has been obtained by applying LJ (12-6-3) potential function. The accuracy of the equation of state has been substantiated by the accuracy of the linear isotherms over the whole range of liquid state where the experimental PVT is available. We also allow the dispersion coefficients of the LJ(12-6-3) potential to be temperature-dependent. This means that the parameters in Eq.6 have more complicated temperature dependence than previous equation of state. From the dispersion coefficients, molecular parameters of the LJ (12-6-3) potential function have been determined. We have suggested general expressions for this temperature dependence and show that they give a good representation of available data for alkali metals. The reduced dispersion coefficients as a function of reduced temperature of the three alkali metals demonstrate the law of corresponding states. This rationalizes the applicability of LJ(12-6-3) potential function for describing the dispersion coefficients of alkali metals.

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