

Research Article

Calculation of Thermal Pressure Coefficient of Lithium Fluid by pVT Data

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For thermodynamic performance to be optimized, particular attention must be paid to the fluid's thermal pressure coefficients and thermodynamics properties. A new analytical expression based on the statistical mechanics is derived for thermal pressure coefficients of dense fluids using the intermolecular forces theory to be valid for liquid lithium as well. The results are used to predict the parameters of some binary mixtures at different compositions and temperatures metal-nonmetal lithium fluid which agreement with experimental data. In this paper, we have used newly presented parameters of analytical expressions based on the statistical mechanics and predicted the metal-nonmetal transition for liquid lithium. The repulsion term of the effective pair potential for lithium shows well depth at 1600 K, and the position of well depth maximum is in agreement with X-ray diffraction and small-angle X-ray scattering.

1. Introduction

Lithium and its compounds have several industrial applications, including heat-resistant glass and ceramics, high strength-to-weight alloys used in aircraft, lithium batteries, and lithium-ion batteries. These uses consume more than half of lithium production. Trace amounts of lithium are present in all organisms. The element serves no apparent vital biological function, since animals and plants survive in good health without it. The lithium ion Li^+ administered as any of several lithium salts has proved to be useful as a mood-stabilizing drug due to neurological effects of the ion in the human body [1–3].

An important concept in physical chemistry concerns the representation of the force between two molecules by means of a potential energy function. In dense systems this is complex because a molecule in a condensed phase is at all times close to several other molecules. The total intermolecular energy is consequently large, and the properties of these states depend strongly on the nature of the intermolecular forces. When several molecules are simultaneously close to each other, their total energy is not exactly equal to the sum of the pair energies, which

would be observed if each pair was isolated. Due to the fact that the relations between the external pressure and the internal pressure properties are known in principle, it is clear that the study of dense systems can provide valuable information about the intermolecular interactions. However, the relation between the intermolecular potential and the measurable properties of a fluid is quite complex. Only a few experimental methods are available for determination of the molecular interactions [4–6]. The most direct methods are relationships among several physical-chemical parameters which by the intermolecular interactions can be obtained.

A relationship that has recently been derived for dense fluids is the internal pressure regularity, which $((\partial E/\partial V)_T/\rho RT)V^2$ is linear with respect to ρ^2 for each isotherm, where $\rho = 1/V$ is the molar density, E is the internal energy, and V is the molar volume [7]. The internal pressure regularity, which was originally devised for normal dense fluids, is based on the cell theory and considers only nearest adjacent interaction. The regularity is applied well to Lennard-Jones fluids whose interaction potential can be modeled rather accurately by the (12–6) powers of inverse of the intermolecular distance. Lennard-Jones potential function suitably describes the interactions

between the molecules of a fluid under the condition that it behaves as a normal fluid. The internal pressure regularity was attempted to calculate the internal pressure by modeling the average configurationally potential energy and then taking its derivative with respect to volume [7, 8].

The other work is an expression which is known as thermal pressure coefficient of dense fluids (Ar, N₂, CO, CH₄, C₂H₆, n-C₄H₁₀, iso-C₄H₁₀, C₆H₆, and C₆H₅-CH₃) [9–15]. Only, pVT experimental data have been used for the calculation of thermal pressure coefficients [16].

The second is a relationship to predict metal-nonmetal transitions in cesium fluid. An accurate empirical potential was found for dense cesium fluid and used to test the applicability of the theory. These theoretical predictions are in good agreement with experimental results [17–20].

The third is the internal pressure of sodium, potassium, and rubidium attempting to predict X-ray diffraction and small-angle X-ray scattering to the range where the compressibility of the interacting electron gas has been theoretically predicted to become negative. Problems have led us to try to establish a function for the accurate calculation of the internal pressure and the prediction of metal-nonmetal transition alkali metals based on the internal pressure [21].

The thermal pressure coefficient is one of the most important fundamental properties; it is closely related to various properties such as internal pressure, sonic velocity, the entropy of melting, isothermal compressibility, isobaric expansibility, and so on. Thus, the study of thermal pressure coefficient could provide a useful basis for understanding the nature of liquid. Since it is normally difficult to obtain the properties by thermodynamic methods and statistical mechanics methods due to the complex interactions among molecules, experimental methods attracted much attention. A lot of experimental data and correlation functions have been obtained in previous research. The thermal pressure coefficient was introduced to calculate different thermodynamic and volumetric properties for a wide range of fluids including polar, nonpolar, refrigerants, and hydrogen-bonded fluids. It has been also applied for metallic liquids mixtures and ionic liquids. The thermal pressure coefficient is used to calculate isothermal compressibility, thermal expansivity, and ultrasonic velocity of fluids. These results were applied widely in industry and would further accelerate the development of thermodynamic theory. Generally the thermal pressure coefficient may be expressed as functions of temperature and volume. Equations of state are often used to study the thermal pressure coefficient. There are two main types for calculation of the thermal pressure coefficient: one is the Virial type and its derivatives; the other is the Van der Waals type and its derivatives [22–24].

In this paper, a new analytical expression which is based on the statistical mechanics is derived for thermal pressure coefficients of dense fluids using the intermolecular forces theory extended to predict intermolecular interactions of lithium liquid. This equation works very well for all types of dense fluids, for densities greater than the Boyle density but for temperatures below twice the Boyle temperature. The regularity was originally suggested on the basis of a simple

lattice-type model applied to a Lennard-Jones (12,6) fluid [25, 26]. In present paper, the new parameters of temperature dependency have been used to predict the metal-nonmetal transition of lithium metal. We also use the new parameters of temperature dependency for calculation of the thermal pressure coefficient (TPC) for liquid lithium by pVT data. In contrast, in Section 2.1, we present a simple method that keeps first-order temperature dependency of parameters in the equation of state versus inverse temperature. Then, thermal pressure coefficient is derived by pVT data. In Section 2.2, the empirical equations of state explicit in the Helmholtz energy as a function of density and temperature have been developed for the representation of experimental data of the thermal pressure coefficient of lithium fluid. In Section 2.3, temperature dependency of parameters has been developed to second order. In Section 2.4, temperature dependency of parameters has been developed to third order, and then thermal pressure coefficient is calculated by pVT data in each state for lithium fluid [16]. In Section 3, it has been shown that a gradual transition from metallic lithium to non-metallic lithium occurs when density decreases [17–21]. While the transition is occurring, a number of changes in the liquid structure happen, since the repulsion term of lithium potential energy versus temperature contains anomalous behavior, and it shows a well depth that the position of well depth maximum is the metal-nonmetal transition region of lithium. In the present paper, we also show that the repulsion branch of the effective pair potential has been used to predict this transition.

2. Theory

A general equation of state which has been recently used for pure dense fluids, according to which $(Z - 1)V^2$ is linear with respect to ρ^2 , each isotherm as

$$(Z - 1)V^2 = A + B\rho^2, \quad (1)$$

where $Z \equiv pV/RT$ is the compression factor, $\rho = 1/V$ is the molar density, and A and B are the temperature-dependent parameters [26, 27]. A typical isotherm (1000 K) is shown in Figure 1, where it has been accepted that the lowest density conserves the linear relation is equal to the Boyle density. All the liquid isotherms are found to be quite linear over almost the entire density range from the vaporization line to the freezing line. For convenience only, the molar densities and volumes have been reduced by the critical value $\rho_C = 14.409 \text{ mol}\cdot\text{L}^{-1}$. In order to find the temperature range over which the linearity holds when $\rho \geq \rho_B$, we have plotted $(Z - 1)V^2$ against ρ^2 for lithium at different temperatures. The results are summarized in Table 1, including the intercept and slope of the fitted straight line, the pressure range of the data, and the average absolute percent deviation of the calculated and predicted densities for a given pressure. Because both $(Z - 1)V^2$ and ρ^2 are subject to experimental error, we also show the coefficient of determination R^2 , which is simply the square of the correlation coefficient. Here, R^2 should be within 0.005 of unity for a straight line to be

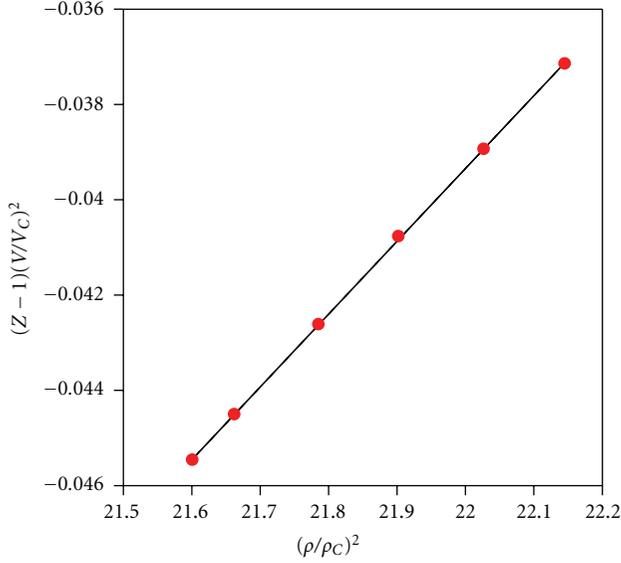


FIGURE 1: Typical isotherm of $(Z - 1)V^2$ versus ρ^2 for liquid Li at 1000 K.

considered a good fit. In such condition we, use the linear isotherm regularity and obtain the external pressure as:

$$\frac{p}{\rho RT} = 1 + A\rho^2 + B\rho^4. \quad (2)$$

2.1. Limitation of Analytical Equation of State by First-Order Temperature Dependency of Parameters. We first calculate pressure by equation of state of the linear isotherm regularity and then use first-order temperature dependency of parameters to get the thermal pressure coefficient for the dense fluid, where

$$\begin{aligned} A &= A_2 - \frac{A_1}{RT}, \\ B &= \frac{B_1}{RT}. \end{aligned} \quad (3)$$

Here, A_1 and B_1 are related to the intermolecular attractive and repulsive forces, respectively, while A_2 is related to the nonideal thermal pressure, and RT has its usual meaning.

In the present paper, the starting point in the derivation is (2). By substitution of (3) in (2), we obtain the pressure for lithium metal fluid:

$$p = \rho RT + A_2 \rho^3 RT - A_1 \rho^3 + B_1 \rho^5. \quad (4)$$

We first derive an expression for thermal pressure coefficient using first-order temperature dependency of parameters. The final result is $\text{TPC}^{(1)}$

$$\left(\frac{\partial p}{\partial T}\right)_\rho = R\rho + A_2 R\rho^3. \quad (5)$$

According to (5), the experimental value of density and value of A_2 can be used to calculate the value of thermal pressure coefficient. Figure 2 shows the experimental values

TABLE 1: Reduced intercept (A) and slope (B) of $(Z - 1)(V/V_C)^2 = A + B(\rho/\rho_C)^2$, the coefficient of determination R^2 , the pressure range 10 to 100 MPa of the data.

T/K	A	B	R^2
600	-0.5692	0.0211	1.0000
700	-0.4981	0.0189	1.0000
800	-0.4465	0.0173	1.0000
900	-0.4064	0.0161	1.0000
1000	-0.3756	0.0153	0.9999
1100	-0.3506	0.0146	1.0000
1200	-0.3306	0.0141	1.0000
1300	-0.3146	0.0138	1.0000
1400	-0.3015	0.0136	1.0000
1500	-0.2913	0.0135	0.9999
1600	-0.2829	0.0135	0.9999
1700	-0.2767	0.0136	0.9999
1800	-0.2721	0.0138	0.9999
1900	-0.2690	0.0141	0.9999
2000	-0.2675	0.0145	0.9999

of the thermal pressure coefficient versus density for Li fluid compared with the thermal pressure coefficient using the LIR⁽¹⁾ at 600 K. The thermal pressure coefficient using the LIR⁽¹⁾ model yields inaccurate results for the liquid phase. Whereas, we predict that deviation concern to be inaccurate values of A_2 . For this purpose we plot A versus $1/T$ that its intercept shows value of A_2 . Figures 3(a) and 3(b) show plots of A and B versus inverse temperature for lithium, respectively. It is clear that A and B versus inverse temperature are not first-order [16].

2.2. Experimental Basis of the New Equation of State. The development of equations of state for calculating the thermodynamic properties of fluids has progressed over the years from simple cubic and virial equations of state to Beattie-Bridgeman and Benedict-Webb-Rubin (BWR) equations, then to the modified BWR (mBWR) and to the fundamental equation of state explicit in the Helmholtz energy. Although the mBWR form can be converted to the Helmholtz energy form, the latter has advantages in terms of accuracy and simplicity. Most modern wide-range, high-accuracy equations of state for pure fluid properties are fundamental equations explicit in the Helmholtz energy as a function of density and temperature. All single-phase thermodynamic properties can be calculated as derivatives of the Helmholtz energy [9–15].

In this paper, we present a simple method of the ideas and the use the thermal pressure coefficient directly in place of using an equation of state to analyze experimental pVT data. The equation of state described in this paper is explicit in Helmholtz energy A' with the two independent variables density ρ and T . The dimensionless Helmholtz energy $\phi = A'/(RT)$ is commonly split into a part depending on the ideal

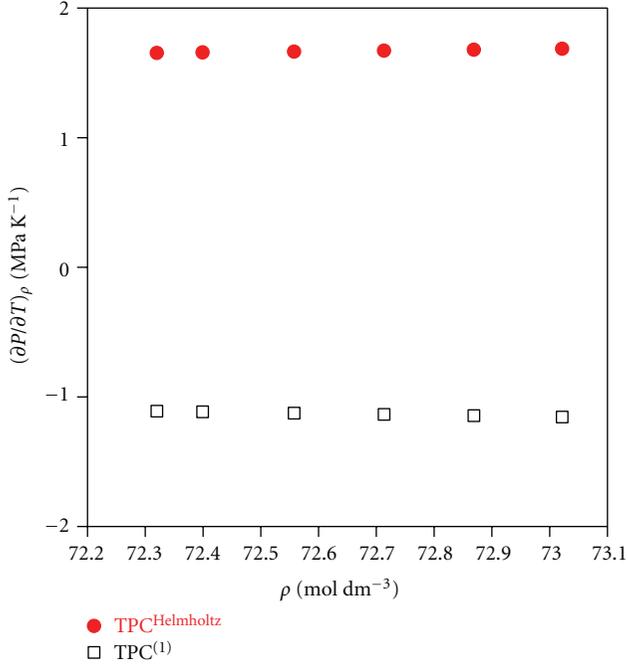


FIGURE 2: The experimental values of thermal pressure coefficient versus density for Li fluid are compared with thermal pressure coefficient using the LIR⁽¹⁾ at 600 K.

gas behavior ϕ^0 and a part which takes into account the residual fluid behavior ϕ^r , namely:

$$\frac{A'(\rho, T)}{RT} = \phi(\delta, T) = \phi^0(\delta, T) + \phi^r(\delta, T). \quad (6)$$

At a given temperature, the pressure can be determined by the Helmholtz energy [4]

$$p(T, \rho) = -\left(\frac{\partial A'}{\partial V}\right)_T. \quad (7)$$

Using the general expression of the relation to the reduced Helmholtz energy $\phi = A'/(RT)$ and its derivatives then gives

$$p^r(\delta, \tau) = 1 + \delta\phi_\delta^r, \quad (8)$$

where $p^r(\delta, \tau) = p(\delta, \tau)/\rho RT$ is the reduced pressure, $\delta = \rho/\rho_C$ is the reduced density, and $\tau = T_C/T$ is the inverse reduced temperature. Both the density ρ and the temperature T are reduced with their critical values ρ_C and T_C , respectively. Since the Helmholtz energy as a function of density and temperature is one of the four fundamental forms of an equation of state, all the thermodynamic properties of a pure substance can be obtained by combining derivatives of the reduced Helmholtz energy ϕ . Here, ϕ_δ and ϕ_δ^r are defined as

$$\begin{aligned} \phi_\delta &= \left(\frac{\partial \phi}{\partial \delta}\right)_\tau, \\ \phi_\delta^r &= \left(\frac{\partial \phi^r}{\partial \delta}\right)_\tau, \end{aligned} \quad (9)$$

that finally, to derive the thermal pressure coefficient, we need only convert the $d\tau$ to dT :

$$d\tau = -\frac{T_c}{T^2} dT. \quad (10)$$

The previous procedure leads to the equation of the thermal pressure coefficient from the reduced Helmholtz energy for real fluids:

$$\left(\frac{\partial p}{\partial T}\right)_\delta = \rho R \left[\left(1 + \delta\phi_\delta^r\right) - \delta\tau \left(\frac{\partial \phi_\delta^r}{\partial \tau}\right)_\delta \right]. \quad (11)$$

2.3. Second-Order Temperature Dependency of Parameters. In order to solve this problem, the linear isotherm regularity equation of state in the form of truncated temperature series of A and B parameters has been developed to second order, and then we obtain thermal pressure coefficient [16]. Figures 4(a) and 4(b) show plots of A and B parameters versus inverse temperature for lithium metal fluid. It is clear that A and B versus inverse temperature are near to second-order equation. Thus, we obtain extending parameters A and B resulted in second-order equation, as

$$\begin{aligned} A &= A_1 + \frac{A_2}{T} + \frac{A_3}{T^2}, \\ B &= B_1 + \frac{B_2}{T} + \frac{B_3}{T^2}. \end{aligned} \quad (12)$$

The starting point in the derivation is (2) again. By substitution of (12) in (2), we obtain the pressure for lithium metal fluid:

$$\begin{aligned} p &= \rho RT + A_1\rho^3RT + A_2\rho^3R \\ &+ \frac{A_3\rho^3R}{T} + B_1\rho^5RT + B_2\rho^5R + \frac{B_3\rho^5R}{T}. \end{aligned} \quad (13)$$

First, second, and third temperature coefficients and their temperature derivatives were calculated from this model, and the final result is for thermal pressure coefficient to form $\text{TPC}^{(2)}$

$$\left(\frac{\partial p}{\partial T}\right)_\rho = \rho R + A_1\rho^3R - \frac{A_3\rho^3R}{T^2} + B_1\rho^5R - \frac{B_3\rho^5R}{T^2}. \quad (14)$$

As (14) shows, it is possible to calculate thermal pressure coefficient at each density and temperature by knowing A_1, A_3, B_1 , and B_3 . For this purpose, we have plotted extending parameters of A and B versus $1/T$ that intercept, and coefficients show the values of A_1, A_3, B_1 , and B_3 . For comparison, Figure 5 shows the experimental values of thermal pressure coefficient versus density for lithium metal fluid that are compared with thermal pressure coefficient using the $\text{TPC}^{(1)}$ and $\text{TPC}^{(2)}$ at 600 K.

2.4. Third-Order Temperature Dependency of Parameters. In another step, we test to form truncated temperature series of A and B parameters to third order. Figures 6(a) and 6(b) show plots of A and B parameters versus inverse temperature

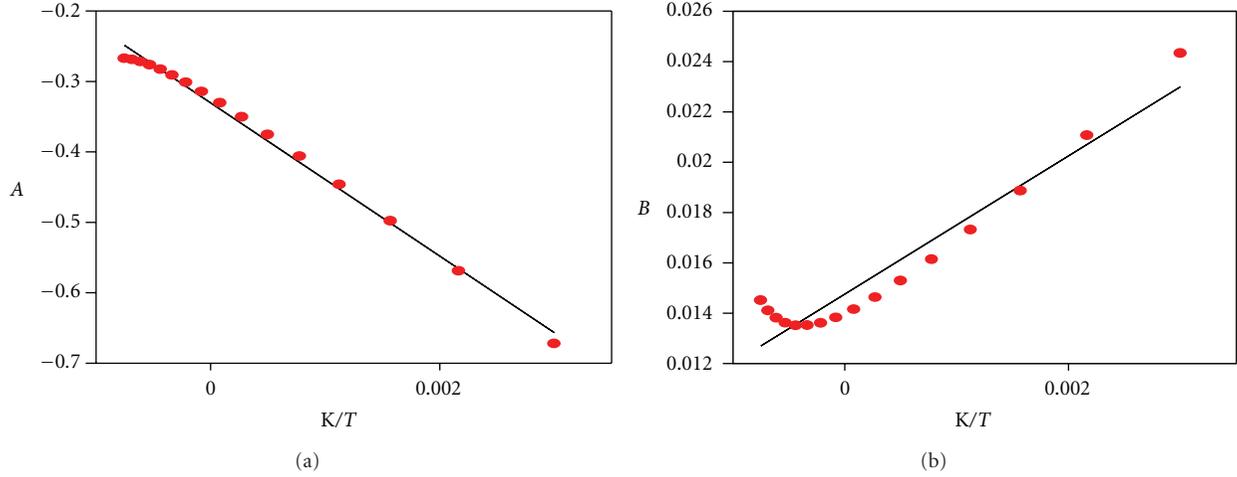


FIGURE 3: (a) Plot of A versus inverse temperature. Solid line is the linear fit to the A data points for Li. (b) Plot of B versus inverse temperature. Solid line is the linear fit for Li.

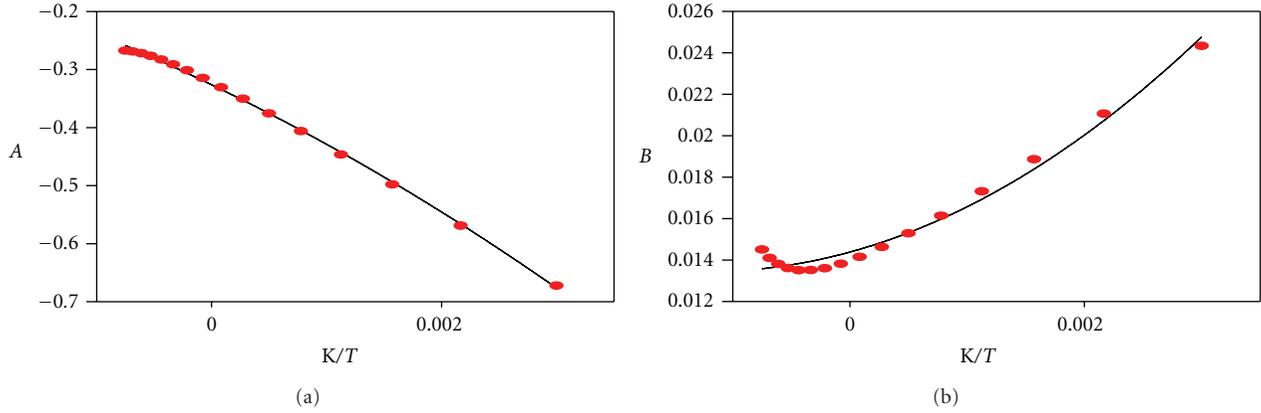


FIGURE 4: (a) Plot of A versus inverse temperature. Solid line is the second-order fit to the A data points for Li. (b) Plot of B versus inverse temperature. Solid line is the second-order fit for Li.

for lithium metal fluid. It is clear that A and B versus inverse temperature are third order

$$\begin{aligned} A &= A_1 + \frac{A_2}{T} + \frac{A_3}{T^2} + \frac{A_4}{T^3}, \\ B &= B_1 + \frac{B_2}{T} + \frac{B_3}{T^2} + \frac{B_4}{T^3}. \end{aligned} \quad (15)$$

The starting point in the derivation is (2) again. By substitution of (15) in (2), we obtain the pressure for lithium metal fluid:

$$\begin{aligned} p &= \rho RT + A_1 \rho^3 RT + A_2 \rho^3 R + \frac{A_3 \rho^3 R}{T} + \frac{A_4 \rho^3 R}{T^2} \\ &+ B_1 \rho^5 RT + B_2 \rho^5 R + \frac{B_3 \rho^5 R}{T} + \frac{B_4 \rho^5 R}{T^2}. \end{aligned} \quad (16)$$

The final result is for thermal pressure coefficient to form $\text{TPC}^{(3)}$

$$\begin{aligned} \left(\frac{\partial p}{\partial T} \right)_\rho &= \rho R + A_1 \rho^3 R - \frac{A_3 \rho^3 R}{T^2} - \frac{2A_4 \rho^3 R}{T^3} \\ &+ B_1 \rho^5 R - \frac{B_3 \rho^5 R}{T^2} - \frac{2B_4 \rho^5 R}{T^3}. \end{aligned} \quad (17)$$

Based on (17), to obtain thermal pressure coefficient, it is necessary to determine values $A_1, A_3, A_4, B_1, B_3,$ and B_4 . For this purpose, we have plotted extending parameters of A and B versus $1/T$ that intercept, and coefficients show the values of $A_1, A_3, A_4, B_1, B_3,$ and B_4 . In contrast, Figures 7 and 8 show the experimental values of thermal pressure coefficient versus density for liquid lithium that are compared with thermal pressure coefficient using the $\text{TPC}^{(1)}$, $\text{TPC}^{(2)}$, and $\text{TPC}^{(3)}$ at 600 and 1600 K, respectively.

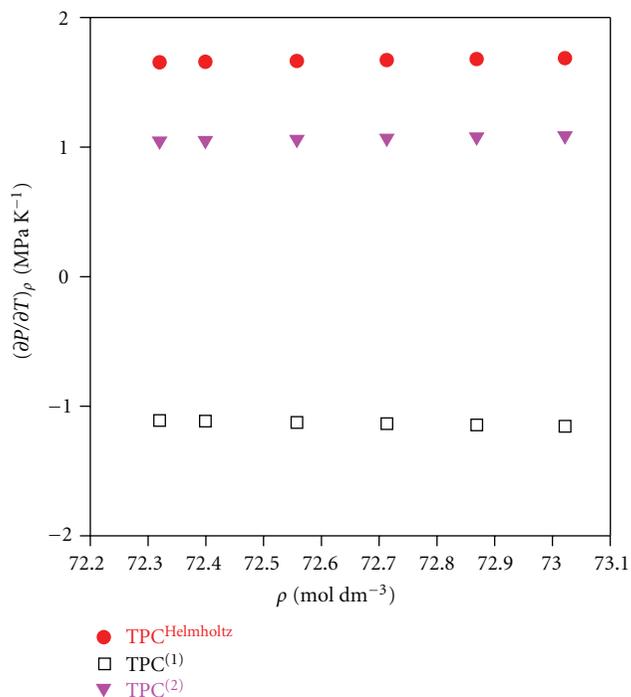


FIGURE 5: The experimental values of thermal pressure coefficient versus density for Li fluid are compared with thermal pressure coefficient using the LIR⁽¹⁾ and LIR⁽²⁾ at 600 K.

3. Prediction of Metal-Nonmetal Transition

Lithium has the highest critical temperature of any fluid alkali metals. Therefore, it has been investigated experimentally with accurate measurements in the liquid region. These measurements involve its magnetic, electrical, structural, optical, and thermophysical properties with optimal control of temperature in the critical region. The fundamental difficulty in dealing with fluid metals is that the electronic structures of liquid and gas phases are completely different [17–21]. The electronic structure of lithium (and other molten metals) at low temperatures can be well approximated by the structure of the free electron gas, and thus the thermodynamic properties of metals can be obtained by the same cohesion mechanism of the free electron gas. Experimental data clearly represent that lithium near 1600 K (at densities larger than $58 \text{ mol} \cdot \text{L}^{-1}$) follows the nearly free electron theory of metals that considers the nuclei completely shielded by delocalized electrons, and it is in agreement with X-ray diffraction and small-angle X-ray scattering. At lower densities ($58 \text{ mol} \cdot \text{L}^{-1}$), the cohesion mechanism of its atoms will be suppressed by a partial localization of electrons, and the metallic character is changed to a nonmetal kind and a gradual metal-nonmetal transition (M-NMT) occurs. Analytical equations of state are presented for fluid lithium in metal, nonmetal, and in metal-nonmetal transition states (Table 1). Equations of state for metal and nonmetal states are simple in form but the complexities of the transition state lead to a complex equation. The interatomic potential function used to describe the metal

state has a soft repulsion wall, and that of the nonmetal state is the same as the potential function of the nonpolar fluid with induced dipole intermolecular interaction. Metal-nonmetal transition occurs in the liquid density range lower than $58 \text{ mol} \cdot \text{L}^{-1}$, and a temperature-dependent interaction potential function, which gradually changes from a pure metal interaction to a nonmetal interaction in the transition region. In accordance with Figure 9, the repulsion term of the linear isotherm regularity equation of state for lithium versus temperature presents well depth that the position of well depth maximum is a temperature-dependent quantity. In the transition region, position of well depth maximum represents that lithium near 1600 K and at densities larger than $58 \text{ mol} \cdot \text{L}^{-1}$ has a singularity characteristic of phase transition. In accordance with Figure 10, we have shown that the attractive term of the isotherms of $(Z - 1)V^2$ against ρ^2 for lithium at different temperatures is not very sensitive to temperature functionality for isotherms at 600–2000 K. In accordance with these observations, we can say which repulsion term of the potential energy of the lithium metal plays the fundamental role in metal-nonmetal transition.

4. Results and Discussion

Lithium is a trace element in the human body [27]. Think of Lithium-ion batteries, and the first things likely to come to mind are cell phones, laptop computers, and other portable electronic gadgets. No doubt about it, the low weight, small size, and large energy capacity of lithium-ion batteries relative to other battery types have helped these high-tech power packs corner the market in the portable electronics arena. These days, the batteries are being used to energize powerful electric drive systems in automobiles and motorcycles. They are also being tapped for medical and backup power services and other applications that demand a big jolt of power [28].

One of the most difficult problems within the context of the thermodynamics lies in the shortage for experimental data for some basic quantities such as thermal pressure coefficients which are tabulated for extremely narrow temperature ranges, normally around the ambient temperature for several types of liquids. Furthermore, the measurements of the thermal pressure coefficients made by different researchers often reveal systematic differences between their estimates. Liquids and dense fluids are usually considered to be complicated on a molecular scale, and a satisfactory theory of liquids only began to emerge in the 1960s. However, they show a number of experimental regularities, some of which have been known by theoretical basis.

A work has led to try to establish a correlation function for the accurate calculation of the thermal pressure coefficients for different fluids over wide temperature and pressure ranges. The most straightforward way to derive the thermal pressure coefficient is the calculation of thermal pressure coefficient with the use of the principle of corresponding states which covers wide temperature and pressure ranges. The principle of corresponding states calls for the reduced thermal pressure at a given reduced temperature

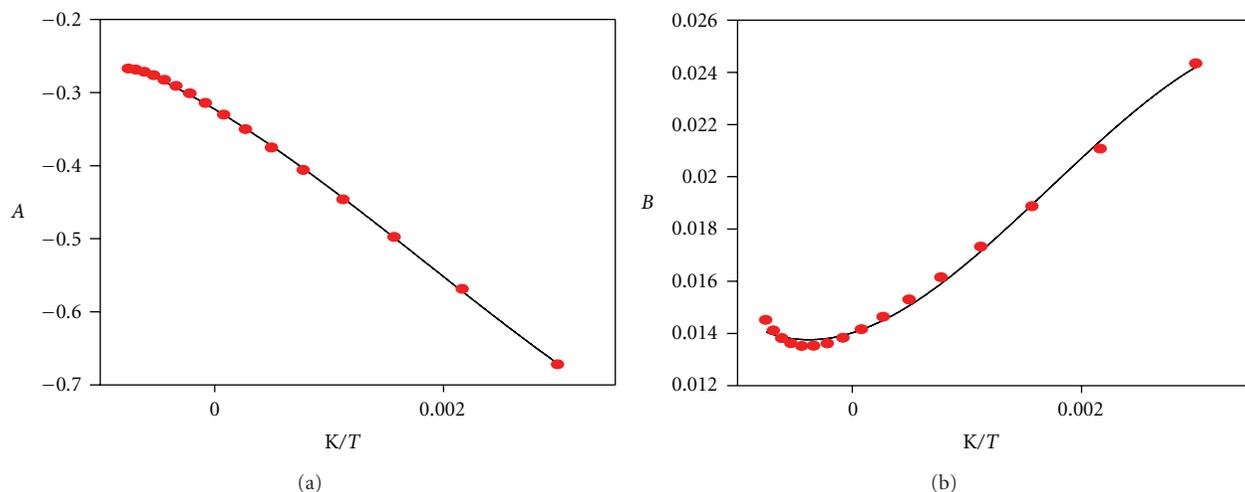


FIGURE 6: (a) Plot of A versus inverse temperature. Solid line is the third-order fit to the A data points for Li. (b) Plot of B versus inverse temperature. Solid line is the third-order fit for Li.

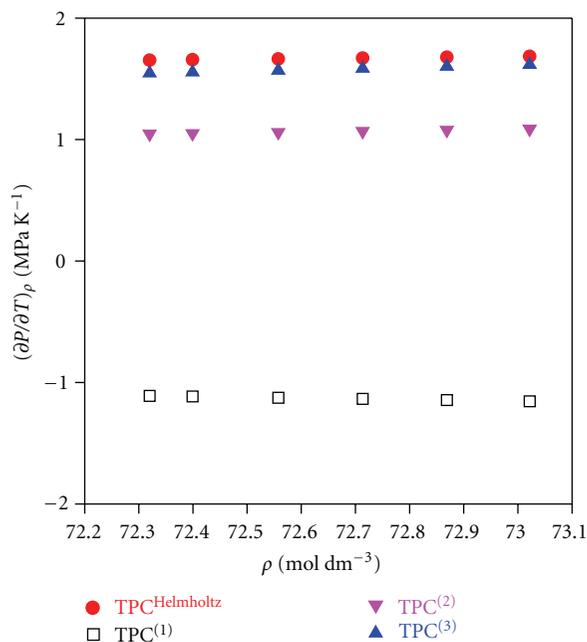


FIGURE 7: The experimental values of thermal pressure coefficient versus density for Li fluid are compared with thermal pressure coefficient using the LIR⁽¹⁾, LIR⁽²⁾, and LIR⁽³⁾ at 600 K.

and density to be the same for all fluids. This is true, since the corresponding-states approach is appropriate for conditions of low density in which the fluid molecules are far apart and thus have little interaction. Moreover, at low density, the gas behaves ideally and its thermal pressure coefficient is temperature independent and approaches ρR in the zero-density limit. However, as density increases, molecular interactions become increasingly important, and the principle of corresponding states fails. The leading term of this correlation function is the thermal pressure

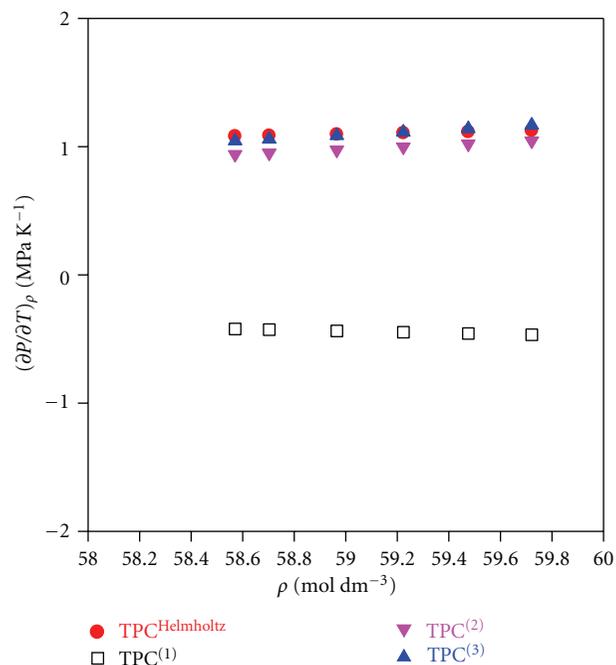
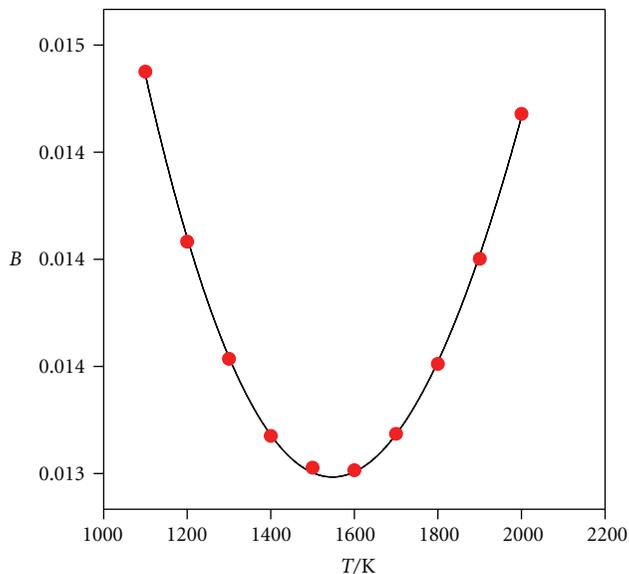
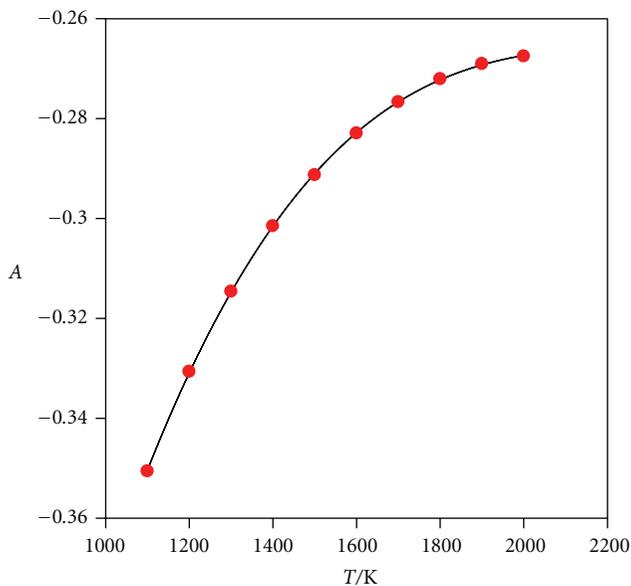


FIGURE 8: The experimental values of thermal pressure coefficient versus density for Li fluid are compared with thermal pressure coefficient using the LIR⁽¹⁾, LIR⁽²⁾, and LIR⁽³⁾ at 1600 K.

coefficient of perfect gas, in which each gas obeys the low density range. Using this condition can predict the thermal pressure coefficient of different supercritical fluids and refrigerants up to densities $\rho \approx \rho_C$. It is found out “empirically” that at high densities, it is possible to apply the principle of corresponding states to different fluids according to the magnitude of their critical densities versus $\rho_C = 10 \text{ mol dm}^{-3}$ [29, 30].

A general regularity was recently reported for dense fluids, both compressed liquids ($T < T_c$) and dense supercritical

FIGURE 9: Plot of the repulsion component B versus temperature.FIGURE 10: Plot of the attraction component A versus temperature.

fluids ($T > T_c$). The regularity is that $(Z - 1)V^2$ is linear in ρ^2 . The regularity was tested for 13 fluids, including nonpolar, polar, hydrogen-bonded, and quantum fluids, and found to be valid for all of them [25]. Experimentally, the regularity holds for liquid isotherms from the vaporization line to the freezing line and for supercritical isotherms for densities greater than the Boyle density and for temperatures less than twice the Boyle temperature. The Boyle temperature, T_B , and Boyle density, $\rho_B = 1/V_B$, are defined in terms of the second virial coefficient, B_2 : $B_2(T_B) = 0$ and $v_B = T_B B_2'(T_B)$, where $B_2' = dB_2/dT$. The purpose of this paper is to examine whether the regularity extends to lithium fluid in metal, nonmetal, and in metal-nonmetal transition states.

The reason for expecting it to hold for mixtures is the success of one-fluid approximations for mixtures, in which mixtures follow the same equation of state as single substances, but with parameters that depend on the mixture composition. In this paper, we derive an expression for a thermal pressure coefficient of lithium metal by extending the linear isotherm regularity [16]. Unlike previous models, it has been shown in this paper that, thermal pressure coefficient can be obtained without employing any reduced Helmholtz energy. Only, pVT experimental data have been used for the calculation of thermal pressure coefficient of lithium metal. Comparison of the calculated values of thermal pressure coefficient using the linear isotherm regularity with the values obtained experimentally shows the validity of the use of the linear isotherm regularity for studying thermal pressure coefficient of lithium metal. In this paper, it has been shown that the temperature dependences of the intercept and slope of using linear isotherm regularity for lithium metal are nonlinear. This problem has led us to try to obtain the expression for the thermal pressure coefficient of lithium metal using the extending of the intercept and slope of the linearity parameters versus inversion of temperature to third order. The thermal pressure coefficients predicted from this simple model are in good agreement with experimental data. The results show that the accuracy of this method is generally quite good. The resulting model predicts accurately the thermal pressure coefficients from the lower density limit at the Boyle density at the triple temperature up to about double the Boyle temperature. These problems have led us to try to establish a function for the accurate calculation of thermal pressure coefficients of the lithium fluid based on linear isotherm regularity equation of state theory. In contrast, Figures 8 and 9 show the experimental values of thermal pressure coefficient versus density for liquid lithium that are compared with thermal pressure coefficient using the $TPC^{(1)}$, $TPC^{(2)}$, and $TPC^{(3)}$ at 600 and 1600 K, respectively. Although all three models capture the qualitative features for lithium of liquid, only the calculated values of thermal pressure coefficient using the $TPC^{(3)}$ model produce quantitative agreement. Tables 2 and 3 present a more test of these models. Although the $TPC^{(2)}$ model yields good results for lithium of liquid, the $TPC^{(3)}$ model is able to accurately predict the thermal pressure coefficient of the liquid.

In this paper, we have also shown that a gradual transition from metallic lithium to nonmetallic lithium occurs when density decreases. This transition occurs in the liquid density range $58 \text{ mol} \cdot \text{L}^{-1}$. An infinite system of electrons in ground state, subject to a very slowly varying external pressure, has slowly varying properties and can be described by a gradient expansion theory. However, when, there is a spatially rapidly varying with density, or there are regions in which the electron density drops to zero (e.g., electrons in covalence form), the density and other properties of the system exhibit additional spatial variations, which it is called metal-nonmetal transition. This paper deals with some general features of systems of electrons in their ground state. Our starting point is an infinite electron gas,

TABLE 2: The predicted calculated values of the thermal pressure coefficient for liquid lithium by (17). ($A_1 = -225.33e - 3, A_3 = -214.22e + 3, A_4 = 46.460e + 6, B_1 = 20.298e - 3, B_3 = 21.892e + 3,$ and $B_4 = -4.9020e + 6$).

T/K	p/MPa	$\rho/\text{Mol}\cdot\text{L}^{-1}$	$(\partial p/\partial T)_\rho/\text{MPa}\cdot\text{K}^{-1}$
600	10	72.3199	1.5458
600	20	72.3991	1.5537
600	40	72.5576	1.5695
600	60	72.7133	1.5852
600	80	72.8689	1.6011
600	100	73.0216	1.6168
700	10	70.9971	1.2065
700	20	71.0807	1.2128
700	40	71.245	1.2253
700	60	71.4092	1.238
700	80	71.5706	1.2506
700	100	71.7305	1.2632
800	10	69.6657	1.2615
800	20	69.7522	1.2689
800	40	69.9251	1.2838
800	60	70.0951	1.2987
800	80	70.2637	1.3135
800	100	70.4308	1.3284
900	10	68.3228	1.3694
900	20	68.4135	1.3785
900	40	68.5951	1.3969
900	60	68.7723	1.415
900	80	68.9496	1.4334
900	100	69.1239	1.4517
1000	10	66.9697	1.4386
1000	20	67.0648	1.4492
1000	40	67.255	1.4707
1000	60	67.4352	1.4913
1000	80	67.6268	1.5135
1000	100	67.8084	1.5349
1100	10	65.6037	1.4533
1100	20	65.7046	1.4653
1100	40	65.9035	1.4892
1100	60	66.0994	1.513
1100	80	66.2939	1.537
1100	100	66.4841	1.5608
1200	10	64.2262	1.421
1200	20	64.3329	1.4339
1200	40	64.5418	1.4594
1200	60	64.7478	1.485

TABLE 3: Same as Table 2, for different temperatures.

T/K	p/MPa	$\rho/\text{Mol}\cdot\text{L}^{-1}$	$(\partial p/\partial T)_\rho/\text{MPa}\cdot\text{K}^{-1}$
1200	80	64.951	1.5107
1200	100	65.1527	1.5365
1300	10	62.8357	1.3535
1300	20	62.9467	1.3667
1300	40	63.1671	1.3934
1300	60	63.3847	1.4202
1300	80	63.5994	1.4471
1300	100	63.8098	1.4738
1400	10	61.4294	1.2621
1400	20	61.5476	1.2758
1400	40	61.781	1.3031
1400	60	62.0101	1.3303
1400	80	62.2363	1.3578
1400	100	62.4582	1.3852
1500	10	60.0086	1.1567
1500	20	60.134	1.1704
1500	40	60.3804	1.1977
1500	60	60.6225	1.2251
1500	80	60.8617	1.2527
1500	100	61.0951	1.2801
1600	10	58.5706	1.0445
1600	20	58.7032	1.0579
1600	40	58.9654	1.0851
1600	60	59.2233	1.1123
1600	80	59.4755	1.1395
1600	100	59.7219	1.1667
1700	10	57.1138	0.9308
1700	20	57.2565	0.9441
1700	40	57.5346	0.9706
1700	60	57.8084	0.9972
1700	80	58.0749	1.0238
1700	100	58.3372	1.0505
1800	10	55.6369	0.8198
1800	20	55.7896	0.8327
1800	40	56.0865	0.8583
1800	60	56.3775	0.8841
1800	80	56.6614	0.9099
1800	100	56.9395	0.9358
1900	10	54.1383	0.7143
1900	20	54.3012	0.7265
1900	40	54.6196	0.7511
1900	60	54.9308	0.7759
1900	80	55.2334	0.8007
1900	100	55.5288	0.8256
2000	10	52.6138	0.6159
2000	20	52.7896	0.6276
2000	40	53.1311	0.6509
2000	60	53.464	0.6745
2000	80	53.7882	0.6981
2000	100	54.1037	0.7219

subject to a sufficiently slowly varying external pressure, P . It is well known that the structure of a dense fluid is essentially a molecular scale problem. In fact, the repulsive forces have an important role in the determination of the fluid structure, and the cohesive or attractive interactions in a fluid only define the fluid volume. The precise meaning of the metal-nonmetal transition is contained in a generalized manner

in the following well-known thermodynamic equations. In conclusion, we have showed that the metal-nonmetal transition of liquid lithium metal can be explained by the repulsion term of the linear isotherm regularity equation of state, where A and B are the linear isotherm regularity parameters that correspond to the attraction and repulsion components of the Lennard-Jones (12–6) potential function. Analytical equations of state are presented for fluid lithium in metal, nonmetal, and in metal-nonmetal transition states. Equations of state for metal and nonmetal states are simple in form but the complexities of the transition state lead to a complex equation for repulsion term of potential energy. Thus, repulsion term for lithium versus temperature shows well depth in agreement with X-ray diffraction and small-angle X-ray scattering that the position of well depth maximum is a temperature-dependent quantity, and it also shows the metal-nonmetal transition residential [17–21].

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