Prediction of the Metal−Non-Metal Transition Using the Linear Isotherm Regularity

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A gradual transition from metallic to non-metallic occurs when density decreases. In the present work a thermodynamic equation of state namely the linear isotherm regularity, LIR, has been used to predict this transition. While the transition is occurring, a number of changes in the liquid structure happen and therefore a deviation from the linearity predicted by the LIR for a single-phase system is observed. The statistical mechanical theory of mixture, along with the LIR, has been used to derive an appropriate equation of state for the mixture of metal and non-metal, after the beginning of the transition. The derived equation of state is found to be $(Z - 1)v^2 = a + b\rho^2 + c\rho$.[4] In our approach only the experimental $p-v-T$ data are required to predict such a transition for liquids Cs, Rb, Na, and Hg. The predictions are in agreement with experimental observations. It is also shown that the transition is neither first order nor second order.

Introduction

Fluid alkali metals are a typical example of a material whose electronic structure depends strongly on the thermodynamic state of the system. The most striking manifestation of this state dependency is the metal−non-metal transition that occurs when the dense liquid is expanded to lower densities. The dense liquid is a metallic conductor in which the interparticle interactions are dominated by the Coulomb potential, whereas the interactions in the non-metallic phase are weak van der Waals forces. Both types of interactions change with the thermodynamic state.

The most accurate dc-conductivity data of the coexisting liquid and vapor phases show that the conductivity drops sharply across the liquid−vapor phase boundary. The experimental data reveal the fact that there is a qualitative relationship between rapid variation in the conductivity and density.[1] It is also suggested that density is the dominating factor governing the metal−non-metal transition.

Because of the technical difficulties associated with the experiments on high-temperature liquids, the study of the metal−non-metal transition, MNMT, has been done only for the liquid metals with low melting and critical points, like Cs and Hg. Also at high temperatures and pressures the usual conductivity measurements are almost impossible under static equilibrium conditions. For this reason, transient methods have been developed to study a few properties of metals with high critical points. However, such techniques are less accurate than the static measurements.[2] Therefore, thermodynamically, using a theoretical method to predict the metal−non-metal transition seems to be required.

In the present work, we have used an equation of state, LIR, to predict the metal−non-metal transition. Of course, because of using the LIR, which is valid for densities greater than the Boyle density,[3] we are able to predict the transition that occurs at densities greater than the Boyle density. Also, the order of the transition has been studied in this work.

Prediction of the Metal−Non-Metal Transition Using the LIR

A general regularity was reported for pure dense fluids,[3] according to which $(Z - 1)v^2$ is linear with respect to ρ^2 for each isotherm as,

$$(Z - 1)v^2 = A + B\rho^2 \tag{1}$$

where Z is the compressibility factor, $\rho = 1/v$ is the molar density, and A and B are the temperature-dependent parameters as follows:

$$A = A'' - \frac{A'}{RT} \tag{2}$$

$$B = \frac{B'}{RT} \tag{3}$$

Here A' and B' are related to the intermolecular attractive and repulsive forces, respectively, while A'' is related to the nonideal thermal pressure and RT has its usual meaning. This regularity holds for densities greater than the Boyle density and temperatures lower than twice that of the Boyle temperature.

Molten alkali metals (Li through Cs) have been shown to be in the domain of the linear regularity that satisfies pure compressed liquids and liquid mixtures.[4] It is also mentioned[4] that as temperature increases, deviation from the linearity predicted by the LIR is observed. It was mentioned that such a deviation is due to the fact that the basic assumption in the LIR derivation (e.g. the nearest neighboring structure of the liquid state) is broken down. We have studied this deviation more precisely in this work and found that such a change in the liquid structure and especially the change in the nearest neighbor structure is related to the MNMT.

Now, we use this point to predict the MNMT and interpret such deviation. In Figure 1 we have shown the linear regularity for different isotherms of Cs.[5] For those isotherms in which the density at any state is greater than 1.2 g cm^{-3}, corresponding to $\rho^2 = 81.51$ mol^2 L^{-2}, the linearity holds very well (see Figure 1a). But for those isotherms including the lower densities the deviation from the linearity is quite obvious (see Figure 1b).

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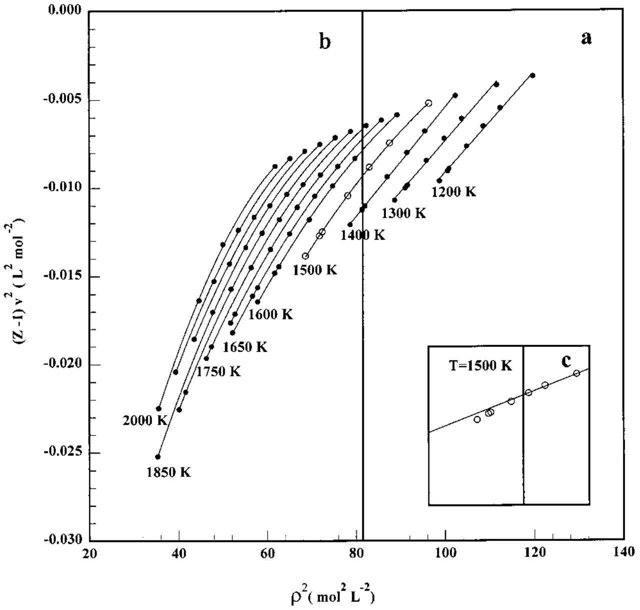

Figure 1. (a) Validity of the linearity of the LIR for different isotherms of Cs before the transition and (b) the deviation from the linearity (quadratic versus ρ^2) after the beginning of the MNMT. (c) Obvious deviation from the LIR for 1500 K isotherm.

The 1500 K isotherm is useful to be focused on, for which the experimental data include both densities lower and higher than 1.2 g cm^{-3}. As shown in Figure 1c, for densities greater than 1.2 g cm^{-3} the linearity holds very well, while deviation from linearity is quite obvious when $\rho < 1.2$ g cm^{-3}. Such a behavior may be related to the transition; in other words, the transition starts when density is around 1.2 g cm^{-3}. Such a claim is in accordance with the conductivity measurement that was used to predict the MNMT. The metal−non-metal transition can be investigated by comparing the measured electrical conductivity with the value calculated from the nearly-free-electron theory.[6] This theory is often used to describe metallic behavior and is valid when the mean free path of the conduction electron is much larger than the average distance between neighboring atoms in the liquid. It has been shown that the nearly-free-electron theory provides a good account of the conductivity for cesium[2] for densities higher than 1.2 g cm^{-3}. According to this theory, the transition begins at 1.2 g cm^{-3} for cesium, which is exactly the density around which the deviation from the LIR is observed. Therefore, by using only $p-v-T$ data along with the LIR we are able to predict the thermodynamic state at which the transition begins. In such a prediction, deviation from the regularity is observed, when density is less than the value at which the transition begins. To interpret such a breakdown in the LIR, we use information of the liquid structure of the metal undergoing the transition. According to which, when density decreases or temperature increases, a number of changes in the pair correlation function, $g(r)$, of metals are observed.[8] First, the intensity of the main peak of $g(r)$ is reduced and broadened, in such a way the average coordination number, Z_c [which is determined by the area of the first peak of $g(r)$], is reduced. Second, the average nearest neighbor distance that is given by the position of the first peak of $g(r)$ increases. However, it is shown that for the range in which the nearly-free-electron model is valid the average coordination number decreases roughly in proportion to the density while the average nearest neighbor distance remains nearly constant. The data analysis of the neutron diffraction measurement of the structural factor shows such a trend for Cs[9] and Rb.[10] Such a behavior for pair correlation is also usually observed for fluids for which the nature of the effective pair potential interaction does not markedly change with liquid density,[8] such as liquid Ar.[10] This simply reveals an important point that, in the liquid thermal expansion, the short-range ordering is reorganized, whereas the average nearest neighbor distance does not change significantly. Such a behavior shows the fundamentally different character of the thermal expansion of liquid and solid.[10] But when the transition begins, the decrease in the average coordination number becomes distinctly smaller, whereas the average nearest neighbor distance gradually increases. These observations clearly demonstrate the interplay between changes in the electronic structure and the thermodynamic and structural properties of the expanded liquid metal. In the derivation of the LIR it is assumed that the coordination number is proportional to density as $Z_c = a\rho$ (where a is a constant), and such an assumption is used to substitute the Z_c with ρ; therefore, the LIR linearity should be broken down when the proportionality constant a changes which means that the transition begins. Therefore the linear regularity of the LIR for an isotherm for which the transition occurs is not expected to hold.

Liquid Behavior after the MNMT

For each isotherm, when the liquid metal expands and reaches a specific density, a gradual MNMT occurs. Then, the conductivity of the system decreases, and the nearly-free-electron theory and the linear isotherm regularity cannot predict the electronic and thermodynamic behavior of the system. It seems that the system has two different states of metal and non-metal as the transition occurs. These two states (metal and non-metal) are characterized by fundamentally two different types of binding. In a metal, the valance electrons are only loosely binded, leading to a monatomic structure with a mobile cloud of electrons with a high electrical conductivity. In contrast, electrons in the non-metal tend to be shared between atoms, resulting in a molecular or polyatomic structure with an insignificant conductivity. If the transition were first order, it would be expected that, after the transition density, the non-metal fluid would obey again from the LIR but with different slope and intercept. In the other words, we would expect to observe only a break in the linearity when the system reaches the density of the transition. But as we mentioned before, the transition occurs gradually and after that different species (monomer, dimer, ...) may exist in the system, in which the mole fraction of each species varies with temperature and density. Such a fluid system may be considered as a mixture of different species of one kind of substance that does not follow from the one-component equation of state. In other words, such a fluid system is expected to follow from the LIR mixture EOS. For simplicity, we consider the metal and non-metal, each of them as a simple species. If we can obtain the system composition while the transition is happening in terms of temperature and density, then it is possible to use the LIR for such a binary mixture to investigate its thermodynamic behavior. A new modeling will be presented in the following section, using the statistical mechanical theory of a mixture along with the LIR to obtain the system composition.

Equation of State for a Mixture of Metal and Non-Metal

Experimentally, the validity of the LIR is examined for dense fluid mixtures.[7] The composition dependencies of the LIR parameters are obtained as well as their temperature dependencies[11] as follows:

$$A_{\text{mix}} = A''_{\text{mix}} - \frac{A'_{\text{mix}}}{RT} \tag{4}$$

$$B_{\text{mix}} = B''_{\text{mix}} - \frac{B'_{\text{mix}}}{RT} \tag{5}$$

$$B_{\text{mix}} = \sum_{ij} B_{ij} x_i x_j \tag{6}$$

$$\left(\frac{A}{B}\right)_{\text{mix}} = \sum_{ij} \left(\frac{A}{B}\right)_{ij} x_i x_j \tag{7}$$

We use the principle of the minimization of free energy at the equilibrium state in order to get the system composition in terms of temperature and density. The Helmholtz free energy of mixture may be obtained by using the LIR and statistical-mechanical theory. The first step to derive the Helmholtz free energy is to obtain the mixture canonical partition function, Q_{mix}, which for a binary mixture is given in the classical limit by a generalized equation, such as

$$Q_{\text{mix}} = [f_1(T)]^{N_1}[f_2(T)]^{N_2} \frac{1}{N_1!N_2!} \int ... \int \exp(-U_N/kT) \mathrm{d}r_1 \, \mathrm{d}r_2 \, ... \, \mathrm{d}r_N$$

where

$$N = N_1 + N_2$$

N_1 and N_2 are the number of species 1 and 2 that form a binary mixture with total number of N. Of course for simplicity, all molecules are assumed to be spherical symmetric. U_N is the configuration energy, which depends not only on the position of the N molecules but also on what may be called the assignment of these species on their positions.[12] Therefore this integral cannot be solved easily because of the dependency of U_N on the assignment of molecules to the N positions of each configuration. To overcome this problem, we construct a model in which there are N molecules at temperature and density exactly the same as that of the real mixture. In our model mixture, we suppose that the average molecular interactions are also the same as that for the real mixture. The only difference between the real and our model mixtures is related to the distinguishability of two kinds of molecules in the real mixture. Then the partition function for this model is

$$Q_{\text{mod}} = [f_1(T)]^{N_1}[f_2(T)]^{N_2} \frac{1}{N!} \int ... \int \exp(-U_N/kT) \, \mathrm{d}r_1 \, \mathrm{d}r_2 \, ... \, \mathrm{d}r_N \tag{8}$$

It is assumed that the molecules are randomly distributed over all assignments. The partition functions of real mixture and the model are related to each other as

$$\frac{Q_{\text{mix}}}{Q_{\text{mod}}} = \frac{N!}{N_1!N_2!} \tag{9}$$

and for the Helmholtz free energy differences, we have

$$F_{\text{mix}}(v,T) - F_{\text{mod}}(v,T) = -kT \ln \frac{Q_{\text{mix}}}{Q_{\text{mod}}} = kT \ln \frac{N_1!N_2!}{N!} \tag{10}$$

Using Stirling's approximation, we obtain the following result for the molar free energy:

$$F_{\text{mix}} = F_{\text{mod}} - RT(x_1 \ln x_1 + x_2 \ln x_2) \tag{11}$$

Therefore the only difference between the Helmholtz free energy of our model and the real mixture is related to the distinguishability of species and hence the entropy of mixing. We emphasize that eq 11 holds for a mixture that obeys the law of the classical mechanics. To obtain F_{mix} in eq 11, we need only the model Helmholtz free energy, F_{mod}. To derive F_{mod}, we use

$$p = kT\left(\frac{\partial(\ln Q)}{\partial v}\right)_{T,N} \tag{12}$$

At constant T and N, we may rearrange this equation to get the partition function of the model as

$$\int \mathrm{d}\ln Q = \int \frac{p}{kT} \mathrm{d}v \tag{13}$$

Using the LIR we have

$$p = \rho RT(1 + A\rho^2 + B\rho^4) \tag{14}$$

Substitution of eq 14 in eq 13 gives

$$\ln Q = N\,(-\ln \rho - A\rho^2/2 - B\rho^4/4 + f(T,N)) \tag{15}$$

Therefore F_{mix} is

$$F_{\text{mix}} = -kT \ln Q = RT[\ln \rho + A\rho^2/2 + B\rho^4/4] + RT \ln[f(T,N)] \tag{16}$$

Comparison of eq 16 with eq 11 reveals that the first term on the right side of eq 16 is the model Helmholtz free energy (note that the second term on the right side of eq 11 is due to the distinguishability of two kinds of molecules in the real mixture). Then we may write

$$F_{\text{mix}} = RT\left[\ln \rho - \frac{A_{\text{mix}}}{2}\rho^2 + \frac{B_{\text{mix}}}{4}\rho^4\right] - RT[x_1 \ln x_1 + x_2 \ln x_2] \tag{17}$$

To obtain the equilibrium composition, the Helmholtz free energy may be minimized with respect to x at constant T and ρ. For simplicity, we assume that the LIR parameters for unlike interactions, A_{12} and B_{12}, are arithmetic means of the corresponding parameters for the pure species. The other assumption is that the A_{mix} is a quadratic function in terms of the system composition. The latter assumption is true for the A'_{mix} but is just an approximation for the A''_{mix}, for which actually a quadratic function was proposed.[11] Using the above-mentioned assumptions, the minimization of the free energy of eq 17 gives the following result for the system composition (mole fraction) as

$$x = \frac{\exp(-C)}{1 + \exp(-C)} \tag{18}$$

where

$$C = \frac{\rho^2}{2}(A_1 - A_2) + \frac{\rho^4}{4}(B_1 - B_2) \tag{19}$$

in which A_1, A_2, B_1, and B_2 are the LIR parameters for two different species. The parameter C is related to the interaction differences of two different species. Because both interactions of two species are related to one substance, the value of C is expected to be small, and hence, we may expand the exponential terms of eq 18 as $\exp(-C) = 1 - C + ...$ To get the final result, we substitute the mole fraction given by eq 18 (after the expansion of the exponential terms) in the LIR EOS for the binary mixture. The following result may be obtained:

$$(Z - 1)v^2 = a + b\rho^2 + c\rho^4 + ... \qquad (20)$$

Here $a-c$ are temperature-dependent parameters as follows:

$$a = {}^1/_2\,(A_1 - A_2)$$

$$b = {}^1/_2\,[(B_1 - B_2) - {}^1/_2\,(A_1 - A_2)^2]$$

$$c = {}^3/_8\,[(B_2 - B_1)(A_1 - A_2)] \qquad (21)$$

Therefore, we may expect that $(Z - 1)\rho^2$ against ρ^2 becomes quadratic for each isotherm, if the terms with higher order than ρ^4 are negligible. Using the experimental $p-v-T$ data, such an expectation will be tested in the following section.

Experimental Test

We have already examined the linearity of the LIR for Cs[5] in Figure 1a, with different isotherms in a dense system before the occurrence of the transition. For the low-temperature isotherms, linearity holds quite well (with the correlation coefficient larger than 0.999). However, when $(Z - 1)v^2$ is plotted versus ρ^2 for an isotherm for which the density is lower than about 1.2 g cm^{-3}, the deviation from linearity is quite obvious (see Figure 1b). As we discussed in the previous section, each isotherm is expected to give $(Z - 1)v^2$ as a quadratic function in terms of ρ^2 when $\rho < 1.2$ g cm^{-3}. As shown in Figure 1b, the agreement between the experiment and the model prediction, eq 20, is very good.

The coefficients in eq 20 are temperature dependent. As predicted by the model (eq 21), the *a* parameter should be linear while the *b* and *c* parameters should be quadratic versus $1/T$, considering the temperature dependencies of the LIR parameters. Figure 2 shows such predictions for Cs. The agreement between the experimental data and the model prediction is quite good.

We have used the experimental data of Rb[13] to examine the linearity. For the reported experimental density range of 1.162−1.465 g cm^{-3}, no deviation from the LIR linearity has been observed (see Figure 3). It is reported that the MNMT for Rb occurs when density is roughly lower than twice the critical density,[2] $\rho_c = 0.347$g cm^{-3}. Therefore, our prediction that MNMT does not happen for Rb in the density range of 1.162−1.465 g cm^{-3} is in accordance with the previous suggestion.[2]

In Figure 4, the validity of the linear regularity is examined for Na. The MNMT has not experimentally been reported for Na in the literature, because of the difficulty of the measurement. However, according to Figure 4, we may suggest that there is no metal−non-metal transition for the density range in which the experimental data are reported.[14]

Figure 5 shows our attempt to study the metal−non-metal transition for Hg.[15] As shown in this figure, the linearity holds very well. Therefore we may suggest that mercury has no such a transition for densities greater than 13 g cm^{-3} (corresponding to $\rho^2 = 4199.3$ mol^2 L^{-2}) . Our suggestion is in agreement with the experimental MNMT for Hg.[16] It is mentioned that the nearly-free-electron theory is in agreement with the experimental conductivity for densities larger than 11 g cm^{-3}. However, the transition happens with further decreasing in density (between 11 and 9 g cm^{-3}).

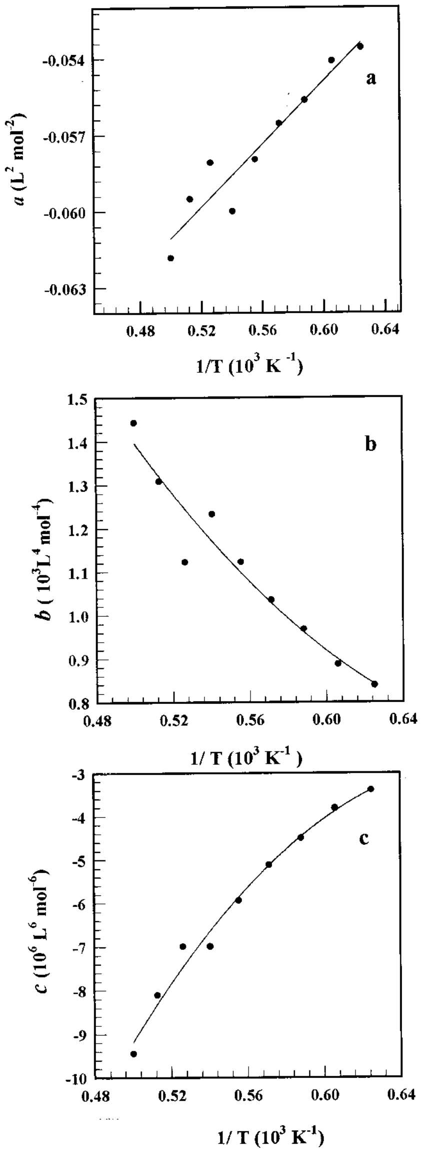

Figure 2. Temperature dependencies of the coefficient of eq 20: (a) *a* is linear versus $1/T$; (b) *b* is quadratic versus $1/T$; (c) *c* is also quadratic against $1/T$.

Order of the Metal−Non-Metal Transition

Most experimental techniques to investigate the metal−non-metal transition monitor the variation of the electrical conductivity with pressure and temperature. The substances for which the conductivity has been studied show a sharp drop close to the critical point for each isotherm. Such a drop in the conductivity indicates that the transition from liquid to vapor has a strong effect on the electronic structure of the metal. Despite the rapid change in the conductivity, there is no indication for a sharp, first-order electronic phase transition except across the liquid−vapor coexistence curve. Such a thermodynamic first-order phase transition (the liquid−vapor transition, LVT) converts high conducting metallic liquid to low conducting vapor. However, such a behavior does not mean that the electronic transition is also first order. As we mentioned before, if the MNMT were sudden and first order, after the transition we would observe a linear isotherm regularity, for which the slope and intercept would be different from those of the liquid metal before the transition. Also, if the transitions were first order we would observe a discontinuity for the first derivations of the free energy (density, entropy) at the transition. But no such a discontinuity is observed; therefore the transition is not first order. If the transition were second order, Gibbs free energy and its first derivatives would be continuous but its

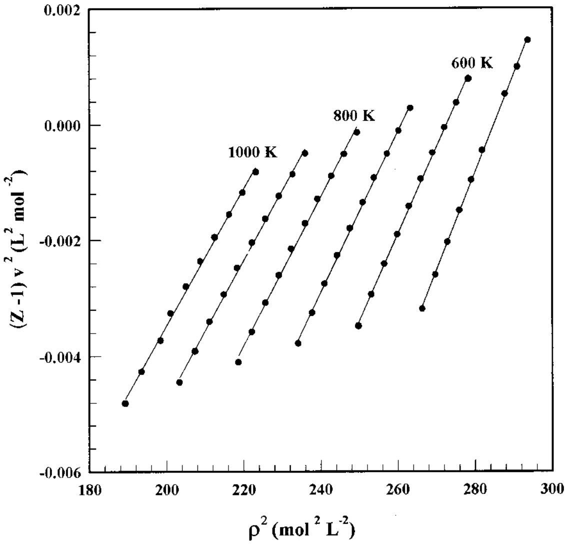

Figure 3. Validity of the LIR linearity for Rb for different isotherms before the MNMT.

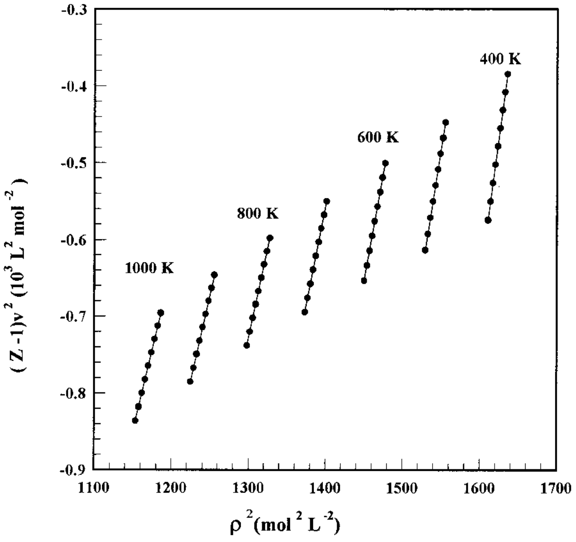

Figure 4. Same as Figure 3 for Na.

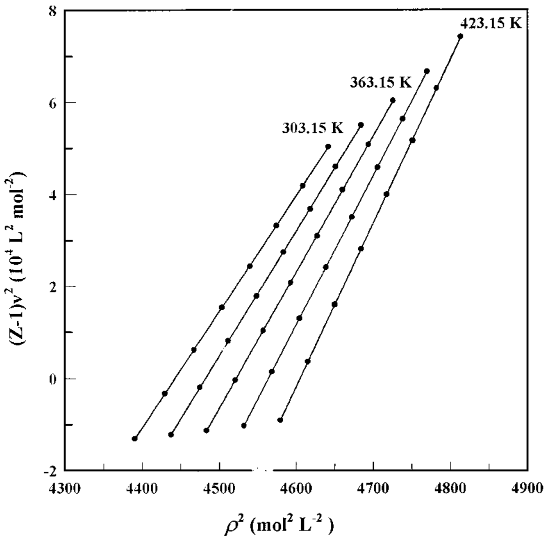

Figure 5. Same as Figure 3 for Hg.

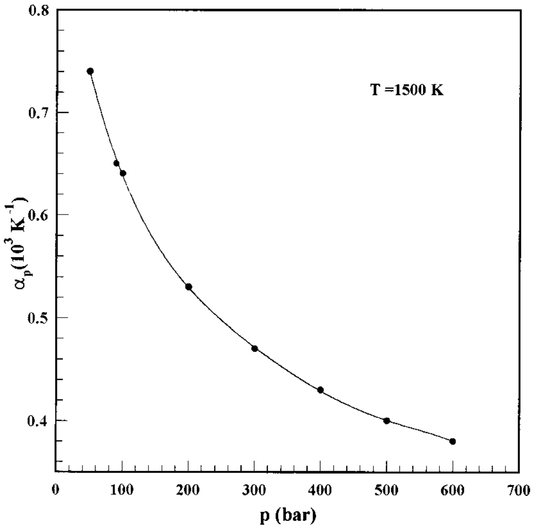

Figure 6. Isobaric expansivity versus pressure for Cs for the density range in which the MNMT happens.

second derivatives such as the isobaric expansivity, α_p, would be discontinuous at the transition. We have plotted α_p versus pressure at constant temperature (1500 K) for Cs[5] for the density range in which the MNMT happens (Figure 6). As shown in this figure, no discontinuity is observed. Therefore we may conclude that the transition is neither first order nor second order.

Conclusion

Liquid metals such as mercury, rubidium, and cesium are electrically conductive at normal conditions. They become non-metallic when expanded to lower densities. The density of an element is the main criteria for its metallic or non-metallic characteristic. Such a conclusion is reasonable, because, for high densities at which the electronic clouds significantly overlap, the valence electrons are expected to be delocalized and hence the metallic characteristic is expected. Even solid H_2 becomes metallic at very high density.[2] There is no definite way to distinguish the metallic and non-metallic states, although some approximate approaches exist. It is found that when the transition occurs, a number of changes in liquid structure happen. For example the proportionality of density to coordination number changes. This fact along with the LIR has been used to predict the transition, because the density is inserted in the LIR instead of the coordination number. The transition starts when deviation from the linearity predicted by the LIR is observed. In this way, our prediction for Cs is in agreement with the experiment (the transition begins at $\rho = 1.2$ g cm^{-3}). For the other metals, in the range of the reported density, Na ($\rho = 0.778-0.930$ g cm^{-3}), Rb ($\rho = 1.62-1.465$ g cm^{-3}), and Hg ($\rho = 13.023-13.091$ g cm^{-3}) no transition happens. Our theoretical method for prediction of the MNMT is very simple and remarkable; since the electronic phase transition is predicted by the LIR, for such a prediction only $p-v-T$ data are needed. Such a prediction shows the power of such a simple EOS, which has also been used to predict many experimentally known regularities and even some new ones.[17,18]

The other fact which has been investigated in this work is the order of the metal−non-metal transition. As we have shown, the order of the transition is certainly neither first order nor second order, at least when such a transition is not simultaneous with the liquid−vapor transition, LVT. If we accept that the nature of the transition does not change with the thermodynamic state, we may say that the transition is neither first order nor second order in every thermodynamic state, even in the liquid−

vapor phase equilibrium. Of course, when the electronic and thermodynamic transitions (MNMT and LVT) occur together, the sudden first-order thermodynamic transition (LVT) influences the electronic transition via a discontinuous change in the density, which leads to a low-density nonconducting vapor. Of course, such an influence dose not mean that there are two independent first-order transitions.

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