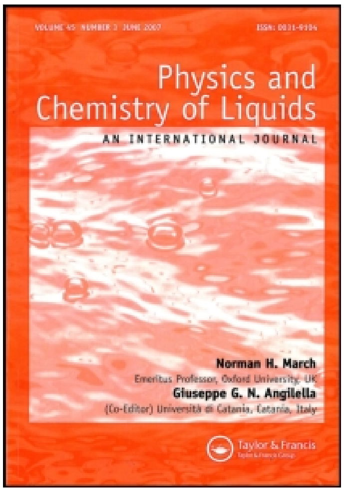

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Temperature and Pressure Dependent Osmotic Pressure in Liquid Sodium-Cesium Alloys

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The evaluation of the osmotic pressure in terms of the concentration fluctuations of mixtures and the equations of state of the pure liquids is considered. The temperature and pressure dependent experimentally measured concentration-concentration correlations in the long wavelength limit of liquid sodium-cesium alloys are used to demonstrate the appreciable dependence of the temperature and pressure on the osmotic pressure as a function of concentration. Introducing interchange energies as functions of temperature and pressure, our analysis is consistent with the Flory model. Thus, a formalism for evaluating the state dependent osmotic pressure is developed and our numerical work is considered to be an extension of the calculations of Rashid and March in the sense that a temperature and pressure dependent interchange energy parameter that more closely parameterizes the state dependent concentration fluctuations in the liquid alloys, is used.

1 INTRODUCTION

It has long been recognized that the simple chemical solution theories can provide a valuable framework for interpreting the thermodynamic properties of binary liquid alloys including non-metallic mixtures. Bhatia *et al.*[1] have used the conformal solution theory[2] to explain the thermodynamic properties including the concentration fluctuations in liquid sodium-potassium alloys. However, the theory could take care of the atomic volume ratio up to 2 and it proved to be inadequate when larger size ratios were considered. In Na-Cs alloys one finds the volume

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ratio approximately equal to 3 and Bhatia and March[3] showed that the Flory model[4] is very useful for such a case.

The aim of this paper is to investigate the behaviour of the osmotic pressure as a function of temperature and pressure. It has recently been pointed out by Rashid and March[5] in extending ideas of March[6] and Hammel,[7] that the osmotic pressure can play an important role when one expresses the thermodynamics of binary liquid mixtures in terms of the thermodynamic properties of pure solvents. Moreover, they plotted the osmotic pressure for various liquid binary mixtures including Na–Cs alloys as a function of concentration.

In order to gain some insights in two-component systems, an interchange energy, W, is usually introduced[8] in the model. The interchange energy is defined as the measure of potential energy increase when one starts from two A–A and B–B pairs of pure liquids and replaces them by two A–B pairs of mixtures. Generally, W is assumed to be independent of temperature and pressure and from the view-points of statistical physics it was not justifiable to take W to be independent of thermodynamic state. It is clear from the analysis of experimental data[9] that a significant temperature dependent $W(T)$ is required. The pressure dependent studies[10] also indicate that, for high external pressure, W depends appreciably on pressure. Thus the variation of external pressure and temperature will influence the osmotic pressure and for achieving such a goal one needs to introduce $W(T, p)$ in the theory.

In Section 2, we present an expression of the osmotic pressure in terms of concentration fluctuations in the liquid mixture and the equations of state of pure liquids. In Section 3, we give the state dependent Flory model and obtain the temperature and pressure dependent interchange energy for liquid Na–Cs alloys.

In Section 4, we represent some of our numerical results and demonstrate that the osmotic pressure depends significantly on the temperature and pressure.

2 THEORETICAL DEVELOPMENT

It has recently been shown that the osmotic pressure is useful in expressing the thermodynamic properties of binary liquid mixtures to those of its pure components. One can start with the molar Gibbs free energy of mixtures, G_m, in terms of the chemical potentials μ_1 and μ_2 of pure constituents 1 and 2 in the mixtures i.e.

$$G_m = (1 - x)\mu_1 + x\mu_2 \tag{2.1}$$

where x is the mole fraction of species 2. If p and T represent the pressure and temperature of the mixture, then the condition for osmotic equilibrium between the mixture and pure component is given by

$$\mu_1^0(T, p - \pi_1) = \mu_1(T, p, x) \tag{2.2}$$

and

$$\mu_2^0(T, p - \pi_2) = \mu_2(T, p, x) \tag{2.3}$$

where the superscript zero and π represent the pure liquid properties and osmotic pressure, respectively.

μ_1 and μ_2 are not independent and from the Gibbs-Duhem relation,[11] one obtains

$$\mu_1 = G_m - x \frac{\partial G_m}{\partial x} \tag{2.4}$$

and

$$\mu_2 = G_m + (1 - x) \frac{\partial G_m}{\partial x} \tag{2.5}$$

From Eq. (2.4) one finds

$$\frac{\partial \mu_1}{\partial x} = -x \frac{\partial^2 G_m}{\partial x^2} \tag{2.6}$$

We know that the concentration fluctuations

$$N\langle(\Delta x)^2\rangle \equiv S_{xx}(0) \tag{2.7}$$

are expressed[1,12] in terms of the second derivaties of the Gibbs free energy of mixture i.e.

$$S_{xx}(0) = \frac{Nk_B T}{(\partial^2 G_m/\partial x^2)_{pT}} \tag{2.8}$$

where k_B and N are the Boltzmann constant and total number of atoms, respectively.

From Eqs (2.6) and (2.8) one can immediately see that

$$\frac{\partial \mu_1}{\partial x} = -x \frac{Nk_B T}{S_{xx}(0)} \tag{2.9}$$

Taking now the concentration derivative of the chemical potential (e.g. Eq. (2.2)) one gets

$$\left(\frac{\partial \mu_1}{\partial x}\right)_{T,p} = -\left[\frac{\partial \mu_1^0(T, p - \pi_1)}{\partial(p - \pi_1)} \frac{\partial \pi_1}{\partial x}\right]_{Tp} \tag{2.10}$$

The first term of the right-hand side of the above equation is by definition the volume i.e.

$$\frac{\partial \mu_1^0(T, p-\pi_1)}{\partial (p-\pi_1)} = V_1^0(p-\pi_1, T) \tag{2.11}$$

of pure liquid 1 at a thermodynamic state $p - \pi_1$, T. This state is surely different from the thermodynamic state of mixture at experiments which are represented by p, T. Thus one can see that the solution characteristic is not only represented by the mole fraction x but also by π_1, which involves solute-solvent interactions. From Eqs (2.9), (2.10) and (2.11) one writes

$$\frac{\partial \pi_1}{\partial x} = \frac{xNk_BT}{S_{xx}(0)V_1^0(p-\pi_1, T)} \tag{2.12}$$

On integrating the above equation one can readily obtain the osmotic pressure π_1 i.e.

$$\pi_1(x) = \int_0^x \frac{xNk_BT}{S_{xx}(0)V_1^0(p-\pi_1, T)}\,\mathrm{d}x \tag{2.13}$$

The evaluation of the osmotic pressure as a function of concentration by iterative procedure is now possible provided the theoretically calculated or experimentally determined values of the concentration fluctuations $S_{xx}(0)$ and the volume, $V_1^0(p - \pi_1, T)$, from the equations of state are inserted in the Eq. (2.13).

π_1 and π_2 are not independent and from the similar arguments an expression for π_2 in terms of $S_{xx}(0)$ and $V_2^0(p - \pi_2, T)$ can also be obtained.

3 TEMPERATURE AND PRESSURE DEPENDENT FLORY'S MODEL

The concentration fluctuations, $S_{xx}(0)$ reveal considerable information about the interaction and structure of binary mixtures and alloys. From the theoretical point of view, several workers[1,3,12] have discussed the characteristic features of $S_{xx}(0)$ on the basis of modelling the expressions for the molar free energy of mixing. It has been said that Bhatia *et al.*[1] have successfully used the regular solution theory in the zeroth approximation[11] for Na-K liquid alloys, where the Gibbs free energy of mixture, G_M, is given by

$$G_M = Nk_BT[x \ln x + (1-x)\ln(1-x)] + N\omega x(1-x) \tag{3.1}$$

The first term in the right-hand side is $(-T)$ times the entropy of mixing and the second term is the heat of mixing. ω is assumed to be a parameter of the model and one usually adjusts this to find agreement with experimental results.

From Eq. (3.1) one can find an expression for $S_{xx}(0)$

$$S_{xx}(0) = \frac{x(1-x)}{1 - Wx(1-x)}, \quad W = \frac{2\omega}{k_B T} \tag{3.2}$$

Here $S_{xx}(0)$ like in the ideal solution results are symmetric about $x = 0.5$ but the magnitude differ from the ideal values depending upon the values of W.

Experimental data[13] of liquid Na–Cs alloys under various temperatures and pressures show appreciable concentration fluctuations occurring at sodium concentration of approximately 0.85 indicating an asymmetry in $S_{xx}(0)$. Bhatia and March[3] realized that the conformal solution theory will be valid if the size difference between the two types of atoms is small i.e.

$$1 < \frac{V_A}{V_B} < 2$$

where V_A and V_B are the atomic volumes, they argued that when the atomic ratio is greater than the condition given above then the two-parameter Flory model[4] is successful in taking the proper account of the thermodynamics of such systems.

The Gibbs free energy of mixing within the model is

$$\begin{aligned} G_M = {} & Nk_B T[x \ln \phi + (1-x) \ln (1-\phi)] \\ & + N\omega(p, T)\phi(1-\phi)[x + (1-x)V_B/V_A] \end{aligned} \tag{3.3}$$

where

$$\phi = \frac{xV_A}{xV_A + (1-x)V_B} \tag{3.4}$$

if $V_A = V_B$ then $\phi = x$ and the expression (3.3) becomes identical with Eq. (3.1).

Introducing now new variables

$$\frac{V_B}{V_A} = r \tag{3.5}$$

and

$$\beta = \frac{r-1}{r} \tag{3.6}$$

one obtains the concentration fluctuations, $S_{xx}(0)$ within the model

$$S_{xx}(0) = \frac{x(1-x)}{1 - x(1-x)f(x)} \tag{3.7}$$

where

$$f(x) = \frac{x + [(1/\beta^3)(1-\beta)W(T,p) - (1/\beta)]}{[(1/\beta) - x]^3} \tag{3.8}$$

It is easily seen from the above equation that when $\beta \to 0$ then $f(x) \to W$. For Na–Cs alloys $\beta = 0.66$ as the ratio of atomic volumes of Cs/Na is 3.

It was argued[9,10] that one can bring consistency in the theoretical description of thermodynamics in liquid alloys by introducing a temperature and pressure dependent interaction parameter. The interaction parameter, W, is found to be a decreasing function of temperature and pressure.

From the study[9] of heat of mixing, one can approximate $W(T)$ by the relation

$$\frac{W(T)}{W(T=0)} = 1 - AT \tag{3.9}$$

with T in degrees Kelvin. In alkali metals the freezing temperature will change only at high pressure (say about 10^4 atm.). The pressure dependent work of Bhatia *et al.*[10] yields

$$\frac{W(p)}{W(p = 1\text{ atm})} = 1 - Bp \tag{3.10}$$

with p in atmospheres and the above equation is found to be valid up to a pressure as large as 10^4 atm.

There are a few experiments[13,14] on $S_{xx}(0)$ under pressure and temperature. Neale and Cusack[13] have reported a reliable temperature and pressure dependent concentration fluctuations in liquid Na–Cs alloys.

We analyzed the data of Neale and Cusack[13] by introducing $W(T, p)$ in the Flory model. The values are

$$W_{1\,\text{atm}}(383\text{ K}) = 1.138, \qquad W_{1\,\text{atm}}(473\text{ K}) = 1.002$$

and

$$W_{383\,\text{K}}(10^3\text{ atm}) = 1.068$$

From the analysis of EMF data on Na–Cs Alblas *et al.*[9] found

$$W_{1\,\text{atm}}\,(384\text{ K}) = 1.04$$

and our findings are consistent with their results and compare well with experimental enthalpy data.[15]

4 NUMERICAL RESULTS FOR THE OSMOTIC PRESSURE

The basic Eq. (2.13) can now be solved by the method of iteration to find $\pi_1(x)$ provided the concentration fluctuations, $S_{xx}(0)$ of the mixture and the equation of state of pure component 1 are given either from experiments or models.

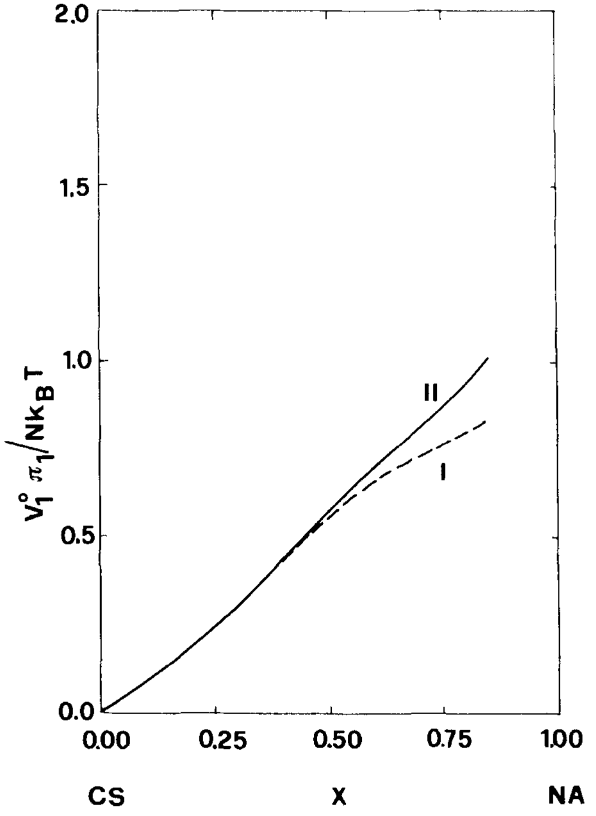

Figure 1 Osmotic pressure π_1 for liquid Na–Cs alloys, curve I is for $p = 1$ bar at $T = 383$ K. Curve II is for $p = 1$ bar at $T = 473$ K.

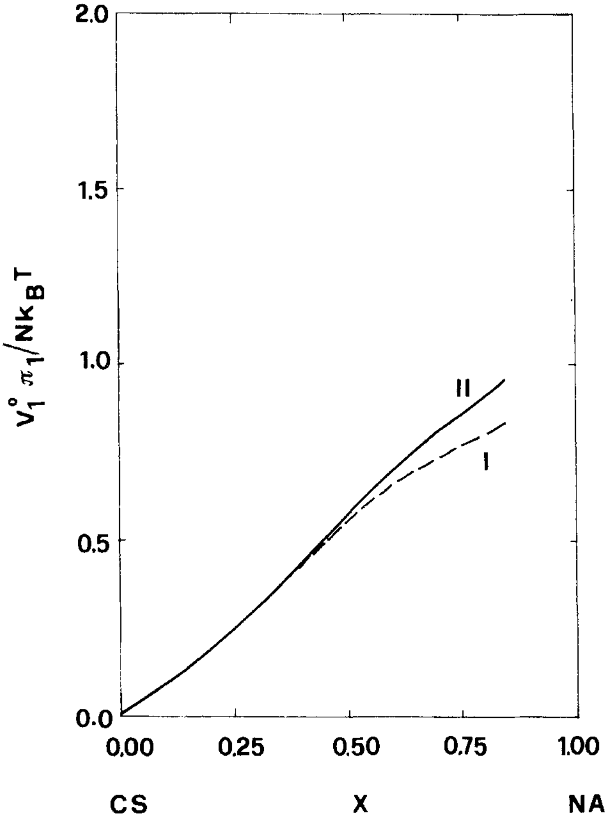

Figure 2 Osmotic pressure π_1 for liquid Na–Cs alloys, curve I is for external pressure equal to 1 bar at temperature equal to 383 K. Curve II is for $p = 10^3$ at $T = 383$ K.

It is known that the dependence of volume on x and p is weak compared to $S_{xx}(0)$ and we used the experimental $S_{xx}(0)$ data[13] to calculate $\pi_1(x)$ as a function of concentration. Figures 1 and 2 show the osmotic pressure of liquid Na–Cs alloys at different temperatures and pressures. We have in fact plotted curves for both $T = 383$ K and $T = 473$ K at 1 bar in Figure 1 whereas in Figure 2 curves are for both $p = 1$ and $p = 10^3$ bar at $T = 383$ K.

The Eq. (2.13) will have physical meaning if $p - \pi_1(x) > 0$, which implies that for external pressure of 10^3 bar at $T = 383$ K and for temperature $T = 473$ K at an external pressure 1 bar the range of physical interest is $0 < x < 0.4$ while for $p = 1$ bar at $T = 383$ K the range lies near $x = 0$. We believe that when experiments are performed at a much higher temperature (say >500 K) and pressure (say $>10^4$

bar) the osmotic pressure $\pi_1(x)$ will become sensitive to pressure and temperature for x values higher than 0.5.

5 CONCLUSION

The Flory model[4] is considered here and the temperature and pressure dependent $W(p, T)$ for Na–Cs liquid alloys are obtained. Our calculations predict values of $W(p, T)$ that are very close to values which are found by other workers. For obtaining $W(p, T)$, a linear pressure and temperature dependent interaction energy is assumed here and a fully consistent theory will include higher powers of pressure and temperature in the expression.

In this article we have tried to understand the nature of the osmotic pressure in Na–Cs liquid alloys at various temperatures and pressures. At present no experiment on liquid metal alloys is performed where one can measure directly the osmotic pressure for such systems. If the situation becomes favourable then our work indicates that the osmotic pressure in Na–Cs liquid metal alloys will play an important role at some higher pressure and temperature say $p > 10^5$ atm and $T > 500$ K.

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