Internal Pressure, Energy of Vaporization and Solubility Parameter of Pb–Sn Molten Binary Mixture at Elevated Temperatures

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Abstract
Internal pressure, excess internal pressure, energy of vaporization, excess energy of vaporization and solubility parameter of Pb–Sn molten binary liquid mixture were calculated over a wide range of temperature and composition. A quantitative treatment has been carried out for these thermodynamic properties with the help of Hildebrand equation. Also, interaction study has been made in the light of excess thermodynamic functions.

Keywords: Molten, internal pressure, elevated temperature, binary mixture, solubility parameter, hildebrand equation.

1. Introduction

The role of internal pressure in liquid solution thermodynamics was recognized by Hildebrand.1–2 The use of this property for a long time was qualitative study of intermolecular forces. Pioneer attempts have been made by several workers3–14 to show the significance and its correlation with other properties. A liquid under a small isothermal volume expansion does work against the cohesive force which causes the change in the internal energy (E). The function \((\partial E/\partial V)_T\) is called internal pressure. Hildebrand1–2 showed that for non polar liquids, \((\partial E/\partial V)_T = n \Delta E_{\text{evap}}/V\), where \(\Delta E_{\text{evap}}\) represents the energy of vaporization of the liquid and \(V\) its molar volume. The quantity \(n\) approaches energy density. For polar liquids \(n\) ranges from 0.32–1.624. Internal pressure and cohesive energy density (c.e.d.), evidently, do not reflect the same physical property of these liquids. Our one of the aim is to analyze the physical significance of internal pressure and cohesive energy density and to demonstrate the usefulness of both properties.

Two liquids do not completely mix if one liquid has much greater cohesion than the other. Conversely, molecules in liquids of similar cohesion are just as likely to interact and mix with each other as with their own kind. Any interaction between unlike molecules enhances the change of miscibility.

Hildebrand1 has referred to the square root of c.e.d. as the solubility parameter because of its frequent use in solubility problems. The internal pressure of Pb–Sn molten binary liquid mixtures were computed from the knowledge of thermal expansion coefficient (\(\alpha\)) and isothermal compressibility (\(\beta_T\)) using Hildebrand equation. Extensive work has been carried out on excess thermodynamic functions like excess internal pressure\(^{15,16}\) and excess energy of vaporization.1 The present work deals with the theoretical prediction of internal pressure of Pb–Sn molten binary systems and its correlation with solubility parameter and energy of vaporization. Variations of these properties with the temperature and composition have been studied quantitatively. All the necessary parameters in the present work were taken from the literature.17 So far as our knowledge is concerned, nobody has made the temperature dependent study of these properties quantitatively.

2. Theoretical

The quantitative relation between solubility parameter and internal pressure has not been completely resol-
The formal definitions of these quantities are:

\[ \delta = \left( \frac{\Delta E}{V} \right)^{1/2} \]  

(1)

\[ P_i = \left( \frac{\partial E}{\partial V} \right)_T = [T(\partial P/\partial T)_V - P] \]

(2)

where \( V, \Delta E, P_i, \delta, \alpha & \beta_T \) are molar volume, energy of vaporization, internal pressure, solubility parameter, thermal expansion coefficient and isothermal compressibility respectively. To relate the two quantities, Hilderbrand proposed the empirical relation as;

\[ P_i = n \frac{\Delta E}{V} = n \delta^2 \]

(3)

For most of the liquids, the atmospheric pressure becomes negligible by compression. Hence,

\[ T \left( \frac{\partial P}{\partial T} \right)_V = \left( \frac{\partial E}{\partial V} \right)_T \]

(4)

The quantity \( \partial P/\partial T \) is equal to \( \alpha / \beta_T \) where \( \alpha \) is the thermal expansion coefficient and \( \beta_T \) is the coefficient of compressibility at constant temperature.

If the phase happens to be an ideal gas, it has been shown that,

\[ \left( \frac{\partial P}{\partial T} \right)_V = \frac{R}{V} \]

(5)

And substitutions of Eq. (5) to Eq. (2), we get,

\[ P = \frac{RT}{V} - \left( \frac{\partial E}{\partial V} \right)_T \]

thus

Rendering \( \partial E/\partial V \) = 0

For a real gas, say a van der Waal’s gas the equation becomes;

\[ \left( \frac{\partial E}{\partial V} \right)_T = a/V^2, \text{ as } \left( \frac{\partial P}{\partial T} \right)_V = R/(V-b) \]

(6)

Moelwyn-Hughes\(^{18}\) analysed Eq.(2) as that pressure of any system consists of two parts; the kinetic pressure, \( T(\partial P/\partial T)_V \), and static pressure, \( (\partial E/\partial V)_T \).

The former is due to intermolecular energy and may be positive and negative. Hence, Eq. (2) applies only to a homogeneous phase. While applying this equation to liquids, many authors\(^{19-24}\) assume \( P \) as atmospheric pressure which is incorrect. In liquids, due to condensed phase, \( (\partial E/\partial V)_T \) should be very high and the kinetic pressure should be low. Hence we can not assume \( P = 0 \). When we consider the effect of temperature, the kinetic pressure should increase with rise temperature and static pressure should decrease as intermolecular forces decrease.

Several workers\(^{23-27}\) discussed a suitable partition functions for liquid and as a result, free volume \( (V_f) \) was given by relation

\[ V_f = \left[ \frac{bRT}{P(V(\partial E/\partial V)_T)} \right]^3 \frac{1}{V^2} \]

(7)

where \( (\partial E/\partial V)_T = P_i \), hence equation becomes

\[ V_f = \left[ \frac{bRT}{P_i} \right]^3 \frac{1}{V^2} \]

(8)

All the notations used in the above equation have there usual significance.

Excess thermodynamic functions have been defined as;

\[ \Lambda^E = \Lambda_{mix} - \Lambda_{ide} \text{ and } \]

\[ \Lambda_{ide} = x_1 A_1 + x_2 A_2 \]

(9)

Where \( \Lambda^E \) is the excess thermodynamic functions, \( \Lambda_{ide} \) is the ideal function and \( \Lambda_{mix} \) is value of liquid mixture respectively.

The internal molar latent heat of vaporization is a measure of the work done against the internal pressure in vaporizing one mole of liquid, occupying volume \( V \), so that,

\[ \left( \frac{\partial E}{\partial V} \right)_T = \Delta E/V \]

### 3. Results and Discussion

Parameters of pure components are listed in Table 1

<table>
<thead>
<tr>
<th>Comp. X</th>
<th>T/K</th>
<th>( \alpha \times 10^4 ) K(^{-1} )</th>
<th>( \beta_T \times 10^9 ) Pa(^{-1} )</th>
<th>( V \times 10^4 ) dm(^3)mol(^{-1} )</th>
<th>( P_i ) kbar</th>
<th>( \Delta E ) K cal</th>
<th>( \delta ) J mole(^{-1} )</th>
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<tr>
<td>Pb</td>
<td>400</td>
<td>1.24533</td>
<td>3.650</td>
<td>19.7351</td>
<td>22.962</td>
<td>10.8410</td>
<td>.0152</td>
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<td></td>
<td>700</td>
<td>12.8993</td>
<td>4.490</td>
<td>20.4172</td>
<td>27.953</td>
<td>13.6536</td>
<td>.0167</td>
</tr>
<tr>
<td>Sn</td>
<td>400</td>
<td>8.8600</td>
<td>2.788</td>
<td>17.3097</td>
<td>21.451</td>
<td>8.8830</td>
<td>.0146</td>
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<td></td>
<td>500</td>
<td>8.9761</td>
<td>2.919</td>
<td>17.5016</td>
<td>23.770</td>
<td>9.9524</td>
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<td>17.7079</td>
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<td>700</td>
<td>9.0997</td>
<td>3.154</td>
<td>17.8910</td>
<td>28.072</td>
<td>12.0151</td>
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</table>

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Table 2: Thermal Expansion Coefficient ($\alpha$), Isothermal Compressibility ($\beta_T$), Molar Volume (V), Internal Pressure ($P_i$), Ideal Internal Pressure ($P_{i,\text{idl}}$), Excess Internal Pressure ($P_{i}^{E}$) of Pb–Sn Molten Binary Mixtures

| Comp X (Pb) | T/K   | $\alpha \times 10^4$ K$^{-1}$ | $\beta_T \times 10^9$ Pa$^{-1}$ | $V_{\text{mix}} \times 10^3$ dm$^3$ mol$^{-1}$ | $P_{i}^{\text{mix}}$ kbar | $P_{i,\text{idl}}$ kbar | $P_{i}^{E}$ kbar | Internal Pressure with composition is not so much prevalent. Excess internal pressure of Pb–Sn liquid mixture also increases as temperature increases. At some places, the value of excess internal pressure decreases i.e. at 700 °C

Table 3: Thermal Expansion Coefficient ($\alpha$), Isothermal Compressibility ($\beta_T$), Molar Volume (V), Energy of Vaporization ($\Delta E_{\text{mix}}$), Ideal Energy of Vaporization ($\Delta E_{\text{idl}}$), Excess Energy of Vaporization ($\Delta E_{i}^{E}$) and Solubility Parameter ($\delta$) of Pb–Sn Molten Binary Mixtures

<table>
<thead>
<tr>
<th>Comp X(Pb)</th>
<th>T/K</th>
<th>$\alpha \times 10^4$</th>
<th>$\beta_T \times 10^9$ Pa$^{-1}$</th>
<th>$V \times 10^3$ dm$^3$ mol$^{-1}$</th>
<th>$\Delta E_{\text{mix}}$ K cal</th>
<th>$\Delta E_{\text{idl}}$ K cal</th>
<th>$\Delta E_{i}^{E}$ K cal</th>
<th>$\delta$ J mole$^{-1}$</th>
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<tr>
<td>10%</td>
<td>400</td>
<td>9.8008</td>
<td>2.909</td>
<td>17.9716</td>
<td>22.674</td>
<td>21.602</td>
<td>0.11</td>
<td>.0151</td>
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<td>600</td>
<td>10.1721</td>
<td>3.180</td>
<td>18.2601</td>
<td>27.925</td>
<td>25.838</td>
<td>0.21</td>
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<td>700</td>
<td>10.1861</td>
<td>3.310</td>
<td>18.4989</td>
<td>29.943</td>
<td>29.943</td>
<td>0.19</td>
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<tr>
<td>20%</td>
<td>400</td>
<td>10.2477</td>
<td>2.960</td>
<td>18.5657</td>
<td>23.299</td>
<td>21.753</td>
<td>0.15</td>
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</tr>
<tr>
<td>600</td>
<td>10.4071</td>
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<td>18.9051</td>
<td>28.016</td>
<td>25.919</td>
<td>0.21</td>
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<td>700</td>
<td>10.4859</td>
<td>3.378</td>
<td>19.0913</td>
<td>30.124</td>
<td>28.049</td>
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<td>30%</td>
<td>400</td>
<td>10.8838</td>
<td>3.110</td>
<td>19.0804</td>
<td>23.552</td>
<td>21.904</td>
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<td>600</td>
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<td>19.3646</td>
<td>28.270</td>
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<tr>
<td>700</td>
<td>11.1502</td>
<td>3.610</td>
<td>19.7649</td>
<td>30.053</td>
<td>28.037</td>
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<tr>
<td>38%</td>
<td>400</td>
<td>10.8234</td>
<td>3.122</td>
<td>19.4623</td>
<td>23.332</td>
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<td>600</td>
<td>11.0136</td>
<td>3.460</td>
<td>19.8551</td>
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<td>700</td>
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<td>29.636</td>
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<tr>
<td>45%</td>
<td>400</td>
<td>11.0988</td>
<td>3.130</td>
<td>19.6461</td>
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<td>11.4169</td>
<td>3.610</td>
<td>20.3146</td>
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<tr>
<td>60%</td>
<td>400</td>
<td>12.7843</td>
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<td>19.8644</td>
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<td>22.357</td>
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<td>13.0263</td>
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<td>20.5627</td>
<td>30.315</td>
<td>27.977</td>
<td>2.33</td>
<td></td>
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</table>

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Pb (10%, 30%, 38% & 80%). These discrepancies have been attributed that in these places interactions between the liquid mixture are much more prevalent. Excess thermodynamic parameter is a measure of the extent of molecular interactions involved in the liquid mixture.

A careful observation of Table 3 reveals that energy of vaporization and solubility parameter increase as temperature increase and these values also increases as composition increases. This is due to the linear relationship of internal pressure with solubility parameter and energy of vaporization.

Thus, the effect of increasing temperature in Eq. 2 is that kinetic pressure always increases and static pressure decreases. In real gases, the thermal pressure is predominant and potential energy is being too small, to be accounted for by a small value of internal pressure. However in liquid system internal pressure is too high to compare with the kinetic molecular motions and there is no method of calculating the pressure of the system to know its quantitative significance. Further, the temperature coefficient of kinetic pressure is most often positive whereas that of internal pressure is negative in liquid systems. Thus Eq. 2 has its roots in gas thermodynamics and is obviously not rigorously applicable to all liquid systems. This clearly explains the discrepancies observed in the computation of internal pressure of Pb–Sn liquid mixture. Variation of internal pressure with composition of Pb at various temperatures are presented in figures 1–3.

We can arrive at a conclusive juncture that Hildebrand’s equation is not sufficient to obtain the internal pressure and allied parameters of liquids and liquid mixtures until its assumption is being modified up to some extent. However, equation is successfully applied to Pb–Sn molten liquid mixture and results obtained are much comparable. Variation of excess thermodynamic functions with temperature becomes powerful tool for predicting the intermolecular interactions in molten liquid mixture.

4. Acknowledgement

Authors are thankful to department of chemistry, V.S.S.D. College, Kanpur and VERSTHEN, a center for research and understanding for their help and support.

5. References


Figure 1: Dependence of the internal pressure $P_i$ on the composition of the Pb–Sn mixture at 400 K. $X_{Pb}$ is the molar fraction of Pb.

Figure 2: Dependence of the internal pressure $P_i$ on the composition of the Pb–Sn mixture at 600 K. $X_{Pb}$ is the molar fraction of Pb.

Figure 3: Dependence of the internal pressure $P_i$ on the composition of the Pb–Sn mixture at 700 K. $X_{Pb}$ is the molar fraction of Pb.
V širokem obsegu sestave ter temperature smo izračunali notranji tlak, presežni notranji tlak, izparilna energija, presežno izparilno energijo ter parametre topnosti za binarne Pb-Sn taline. Navedene termodinamske količine smo obravnavali s pomočjo Hildebrandove enačbe. Iz vrednosti presežnih količin smo skleptali na interakcije v preiskanem sistemu.