

Short communication

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, $(\partial E/\partial V)_T = n \Delta E_{\text{vap}}/V$, where ΔE_{vap} 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 (α) and isothermal compressibility (β_T) using Hildebrand equation. Extensive work has been carried out on excess thermodynamic functions like excess internal pressure¹⁵⁻¹⁶ 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 resolved.

ved. The formal definitions of these quantities are;

$$\delta = (\Delta E/V)^{1/2} \quad (1)$$

$$P_i = (\partial E/\partial V)_T = [T(\partial P/\partial T)_V - P] \quad (2)$$

$$P_i = [\alpha T/\beta_T - P]$$

where V , ΔE , P_i , δ , α & β_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;

$$P_i = n \Delta E/V = n\delta^2 \quad (3)$$

For most of the liquids, the atmospheric pressure becomes negligible by compression.¹³ Hence,

$$T(\partial P/\partial T)_V = (\partial E/\partial V)_T \quad (4)$$

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

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

$$(\partial P/\partial T)_V = R/V \quad (5)$$

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

$$P = RT/V - (\partial E/\partial V)_T \text{ thus}$$

$$\text{Rendering } (\partial E/\partial V)_T = 0$$

For a real gas, say a vander Waal's gas the equation becomes;

$$(\partial E/\partial V)_T = a/V^2, \text{ as } (\partial P/\partial T)_V = R/(V-b) \quad (6)$$

Moelwyn-Hughes¹⁸ 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

$$V_f = \left[\frac{bRT}{PV(\partial E/\partial V)_T} \right]^3 1/V^2 \quad (7)$$

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

$$V_f = \left[\frac{bRT}{P_i} \right]^3 1/V^2 \quad (8)$$

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

Excess thermodynamic functions have been defined as;

$$A^E = A_{\text{mix}} - A_{\text{ide}} \text{ and} \quad (9)$$

$$A_{\text{ide}} = x_1 A_1 + x_2 A_2$$

Where A^E is the excess thermodynamic functions, A_{ide} is the ideal function and A_{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,

$$(\partial E/\partial V)_T = \Delta E/V$$

3. Results and Discussion

Parameters of pure components are listed in Table 1 where as parameters of Pb–Sn molten binary liquid mixtures are presented in Tables 2–3. Values of density, ther-

Table 1: Thermal Expansion Coefficient (α), isothermal compressibility (β_T), Molar Volume (V), Internal Pressure (P_i), Energy of Vaporization (ΔE) and Solubility Parameter (δ) of Pb–Sn molten Liquids

Comp. X	T/K	$\alpha \times 10^5$ K ⁻¹	$\beta_T \times 10^9$ Pa ⁻¹	$V \times 10^3$ dm ³ mol ⁻¹	P_i kbar	ΔE K cal	δ J mole ⁻¹
Sn	400	8.8600	2.788	17.3097	21.451	8.8830	.0146
	500	8.9761	2.919	17.5016	23.770	9.9524	.0154
	600	8.9986	3.050	17.7079	25.757	10.9115	.0161
	700	9.0997	3.154	17.8910	28.072	12.0151	.0168
Pb	400	12.4533	3.650	19.7351	22.962	10.8410	.0152
	600	12.7670	4.195	20.1441	26.569	12.8038	.0163
	700	12.8993	4.490	20.4172	27.953	13.6536	.0167

Table 2: Thermal Expansion Coefficient (α), Isothermal Compressibility (β_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	$\alpha \times 10^5 \text{ K}^{-1}$	$\beta_T \times 10^9 \text{ Pa}^{-1}$	$V_{\text{mix}} \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$	$P_{i(\text{mix})} \text{ kbar}$	$P_{i(\text{idl})} \text{ kbar}$	$P_i^E \text{ kbar}$
10%	400	9.8008	2.909	17.9716	22.674	21.602	0.11
	600	10.1721	3.180	18.2601	27.925	25.838	0.21
	700	10.1861	3.310	18.4989	29.943	29.943	0.19
20%	400	10.2477	2.960	18.5657	23.299	21.753	0.15
	600	10.4071	3.243	18.9051	28.016	25.919	0.21
	700	10.4859	3.387	19.0913	30.124	28.049	0.21
30%	400	10.8838	3.110	19.0804	23.552	21.904	0.16
	600	11.0427	3.410	19.3646	28.270	26.000	0.21
	700	11.1502	3.610	19.7649	30.053	28.037	0.20
38%	400	10.8234	3.122	19.4623	23.332	22.026	1.30
	600	11.0136	3.460	19.8551	27.789	26.066	1.72
	700	11.0869	3.640	20.0838	29.636	28.027	1.60
45%	400	11.0988	3.130	19.6461	23.864	21.131	1.73
	600	11.2993	3.500	20.0899	28.184	26.122	2.06
	700	11.4169	3.610	20.3146	30.105	28.019	2.08
60%	400	12.7843	3.350	19.8644	25.683	22.357	3.32
	600	13.3438	3.850	20.3146	30.258	26.244	4.01
	700	13.6071	4.100	20.5791	32.292	28.001	4.29
80%	400	12.5712	3.425	19.8432	24.702	22.659	2.04
	600	12.9543	3.920	20.2769	28.849	26.406	2.44
	700	13.0263	4.181	20.5627	30.315	27.977	2.33

mal expansion coefficient and molar volume have been taken from the literature.¹⁷

A careful perusal of Table 2 reveals that internal pressure increases as temperature increases. Variation of

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 (α), Isothermal Compressibility (β_T), Molar Volume (V), Energy of Vaporization (ΔE_{mix}), Ideal Energy of Vaporization (ΔE_{idl}), Excess Energy of Vaporization (ΔE^E) and Solubility Parameter (δ) of Pb–Sn Molten Binary Mixtures

Comp X (Pb)	T/K	$\alpha \times 10^5 \text{ K}^{-1}$	$\beta_T \times 10^9 \text{ Pa}^{-1}$	$V \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$	$\Delta E_{\text{mix}} \text{ K cal}$	$\Delta E_{\text{idl}} \text{ K cal}$	$\Delta E^E \text{ K cal}$	$\delta \text{ J mole}^{-1}$
10%	400	9.8008	2.909	17.5522	9.749	9.071	0.678	.0151
	600	10.1721	3.180	17.9515	12.199	11.992	0.207	.0167
	700	10.1861	3.310	18.1436	13.251	12.997	0.254	.0173
20%	400	10.2477	2.960	17.7948	10.348	9.261	1.087	.0153
	600	10.4071	3.243	18.1951	12.671	11.282	1.389	.0167
	700	10.4859	3.387	18.3962	13.759	12.344	1.415	.0174
30%	400	10.8838	3.110	18.0373	10.751	9.452	1.299	.0153
	600	11.0427	3.410	18.4387	13.097	11.469	1.628	.0168
	700	11.1502	3.610	18.6489	14.210	12.509	1.701	.0173
38%	400	10.8234	3.122	18.2338	10.863	9.608	1.255	.0153
	600	11.0136	3.460	18.6361	13.120	11.621	1.499	.0167
	700	11.0869	3.640	18.8535	14.240	12.641	1.599	.0172
45%	400	11.0988	3.130	18.4011	11.216	9.742	1.474	.0154
	600	11.2993	3.500	18.8042	13.546	11.751	1.795	.0168
	700	11.4169	3.610	19.0278	14.631	12.755	1.876	.0174
60%	400	12.7843	3.350	18.7649	12.205	10.037	2.168	.0160
	600	13.3438	3.850	19.1696	14.758	12.036	2.722	.0174
	700	13.6071	4.100	19.4067	15.898	13.000	2.898	.0180
80%	400	12.5712	3.425	19.2500	11.726	10.435	1.291	.0157
	600	12.9543	3.920	19.6568	13.994	12.418	1.536	.0170
	700	13.0263	4.181	19.9119	14.913	13.327	1.586	.0174

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

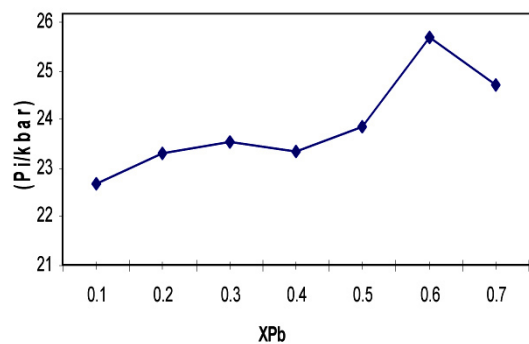


Figure 1: Dependence of the internal pressure P_i on the composition of the Pb–Sn mixture at 400 K. XPb is the molar fraction of Pb.

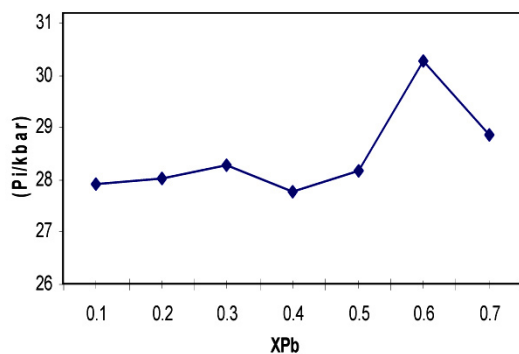


Figure 2: Dependence of the internal pressure P_i on the composition of the Pb–Sn mixture at 600 K. XPb is the molar fraction of Pb.

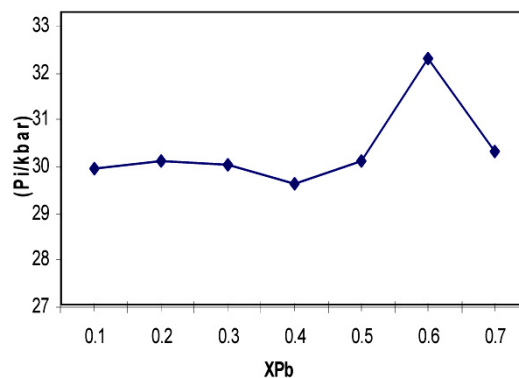


Figure 3: Dependence of the internal pressure P_i on the composition of the Pb–Sn mixture at 700 K. XPb is the molar fraction of Pb.

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.

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5. References

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Povzetek

V širokem obsegu sestave ter temperature smo izračunali notranji tlak, presežni notranji tlak, izparilno 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 sklepali na interakcije v preiskovanem sistemu.