Volume of Mixing in the Liquid Bismuth-Lead System

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Synopsis. The results obtained in determining the volume of mixing v^m in the liquid Bi-Pb system at 660 K using the pycnometer method indicate the compound Pb_3Bi_2 at the composition 0.6. The shifting of the slight positive v^m_{max} to the composition 0.4 is attributed to a nonlinear Wagner effect.

The behavior of liquid metallic systems has not yet been thoroughly explored. The theoretical relationships between the thermodynamic functions of metallic mixtures were derived for simple models e.g, the theory by Prigogine[1] which gives the relation of the volume of mixing to the enthalpy of mixing but could not illustrate the behavior of mixing in the liquid bismuth-lead system[2] or other of complicated behaviors.

In the present investigation we report the results obtained in determining the volume of mixing in the liquid Bi-Pb system at 660 K by using the pycnometer method since these results could shed light on the behavior of mixing in the Bi-Pb system and other related binary ones.

Experimental

The metal used were of extra purity grade (E. Merck Company). The experimental procedures adopted were similar to those used earlier.[3] The apparatus employed was a slightly modified version of the type used by Wittig and Huber.[3] Argon gas was used as a protector in order to avoid oxidation.

Theory and Procedure. The additional behavior y^{ad} is given by

$$y^{ad}=y_1^\circ+(y_2^\circ-y_1^\circ)\,x_2 \tag{1}$$

where y_1° and y_2° are the values of the molar quantities of the components 1 and 2, respectively and x_2 the mole fraction of the component 2. The form function of the excess function, X^y is given through the equation

$$X^y(x_2) = \frac{y^e}{x_2(1-x_2)} \tag{2}$$

y^e refers to the excess quantity. The excess volume and partial excess volumes can be expressed as polynomial functions:

$$v^e(x_2) = \sum_{k,l} a_{kl}\,x_2^k = \sum_{k,l} a_{kl}\,x_2^k\,(1-x_2)^l \tag{3}$$

$$v_1^e(x_2) = \sum_{k,l} (1-k)\,a_{kl}\,x_2^k \tag{4}$$

$$v_2^e(x_2) = \sum_{k,l} (1-k)\,a_{kl}\,x_2^k + \sum_{k,l} k\,a_{kl}\,x_2^{k-l}. \tag{5}$$

The density d has been computed at the temperature of measurement ϑ from the mass m and the volume of the pycnometer V_{py} as follows:

$$d=m/V^{22.9}\cdot[1+3a(\vartheta-22.9)], \tag{6}$$

where 22.9 °C is the calibration temperature of the pycnometer and a the thermal coefficient of silica glass which is given by

$$a_{SiO_2}=0.59\times10^{-6}\,K^{-1}. \tag{7}$$

Results and Discussion

Results of the density determinations are presented in Table 1. The results have been least squares fitted by the following polynomial expression:

$$d(x_2)=9.9297+0.5003\,x_2+0.2332\,x_2^2-0.0769\,x_3^3. \tag{8}$$

The standard deviation is 0.02% for a single measurement.

In Table 2 are collected the values of the average molar volume of the mixture of Bi-Pb as found in the present study. The results have been least squares fitted by a polynomial expression with a standard deviation of 0.012% for a single measurement. The polynomial expression is given by

$$v(x_2)=21.0458-1.2445\,x_2-0.4103\,x_2^2+0.1805\,x_3^3 \tag{9}$$

Table 3 represents the values of the integral and partial molar volume of mixing as determined in the present study. The volume of mixing can be calculated according to the following equation:

$$v^m=v-v^{ad}=v-v_1^\circ+x_2(v_2^\circ-v_1^\circ) \tag{10}$$

Table 1. Experimentally Determined Densities ($\times10^{-3}$) for Liquid Lead-Bismuth at 660K in $kg\,m^{-3}$. Estimated Standard Deviations in Parenthesis

x_2	d	x_2	d
0	9.9318(21)	0.6	10.2994(15)
0.1	9.9839(20)	0.7	10.3656(21)
0.2	10.0404(20)	0.8	10.4417(20)
0.3	10.0967(20)	0.9	10.5148(21)
0.4	10.1643(21)	1.0	10.5882(20)
0.5	10.2305(20)		

Table 2. Average Molar Volumes ($\times10^6$) for the Mixture Bi-Pb in $m^3\,mol^{-1}$. Estimated Standard Deviations in Parenthesis

x_2	v	x_2	v
0	21.0483(25)	0.6	20.1929(26)
0.1	20.9200(26)	0.7	20.0378(23)
0.2	20.7844(25)	0.8	19.8774(25)
0.3	20.6429(26)	0.9	19.7229(25)
0.4	20.4913(26)	1.0	19.5737(23)
0.5	20.3410(25)		

Table 3. Integral and Partial Molar Volume of Mixing ($\times 10^6$) for the Liquid Bi-Pb System at 660 K in $m^3 mol^{-1}$. Estimated Standard Deviations in Parenthesis

x_2	v^m	v_1^m	v_2^m
0	0.0022(22)	0.0000	0.2297
0.1	0.0213(24)	0.0037	0.1569
0.2	0.0285(23)	0.0135	0.1009
0.3	0.0348(24)	0.0272	0.0595
0.4	0.0353(24)	0.0425	0.0308
0.5	0.0325(23)	0.0575	0.0123
0.6	0.0267(23)	0.0697	0.0021
0.7	0.0240(24)	0.0772	−0.0019
0.8	0.0112(23)	0.0778	−0.0022
0.9	0.0035(24)	0.0692	−0.0008
1.0	0.0024(24)	0.0493	0.0000

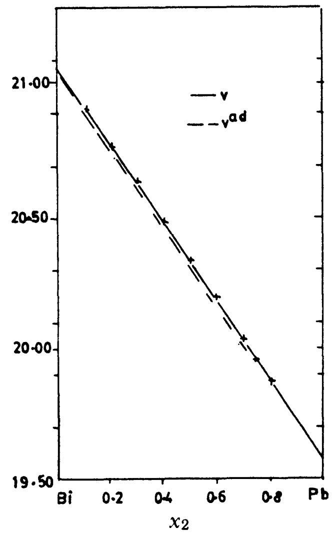

Fig. 1. Average molar volume, v, and additional volume, v^{ad}, for the mixture Bi-Pb.

where v_1° and v_2° are the molar volumes of the pure components 1 and 2, respectively. Figure 1 shows the average molar volume of the mixture, v and the additional volume v^{ad}. For the volume of mixing, the following polynomial expression is derived:

$$v^m = 0.2298\, x_2 - 0.4103\, x_2^2 + 0.1805\, x_2^3 \tag{11}$$

The partial molar volume of mixing of bismuth and lead are given through the following equations:

$$v_1^m = 0.04103\, x_2^2 - 0.3610\, x_2^3 \tag{12}$$

$$v_2^m = 0.2298 - 0.8206\, x_2 + 0.9518\, x_2^2 - 0.3610\, x_2^3 \tag{13}$$

As illustrated in Table 3, the estimated standard deviation (esd.) is not larger than expected from the pycnometer measurement uncertainties, 2.2×10^{-9}, 2.4×10^{-9} $m^3 mol^{-1}$. The plot of v^m versus the mole fraction x_2 is shown in Fig. 2. It is clearly observable that v^m takes slight positive values. The curve of v^m against x_2 and those of v_{Bi}^m and v_{Pb}^m point out to the existence of a compound. This was also recognized from the behavior of the enthalpy and free enthalpy in this system.[4)]

According to the Wagner effect,[5)] the compound will be formed as follows: 3 Pb+2 Bi=Pb_3Bi_2. The composition of the compound and also that of the maximum of the volume of mixing, v_{max}^m, will be: 1−2/(2+3)=0.6. However, the Wagner effect requires sufficiently large difference in electronegativity between the acceptor (Bi) and the donor (Pb). In fact, the electronegativity difference between Bi and Pb (0.1—0.12) is not large enough. This could be a reason for the shifting of the maximum of the volume of mixing from the composition 0.6 to 0.4 (Fig. 2). This means that we have here to deal with a nonlinear Wagner effect as found in the systems Zn-Sb[7)] and Cd-Bi.[8)] A second possibility of the existence of a compound at the composition 0.4 (the composition of v_{max}^m) still remains under investigation.

Table 4. The Form Function of the Volume of Mixing ($\times 10^6$) for the Liquid Bi-Pb System at 660 K in $m^3 mol^{-1}$. Estimated Standred Deviations in Parenthesis

x_2	X^v	x_2	X^v
0	0.2323(26)	0.6	0.1194(20)
0.1	0.2137(20)	0.7	0.1059(25)
0.2	0.1912(20)	0.8	0.0833(20)
0.3	0.1781(25)	0.9	0.0698(25)
0.4	0.1597(22)	1.0	0.0492[a)]
0.5	0.1372(23)		

a) Calculated value.

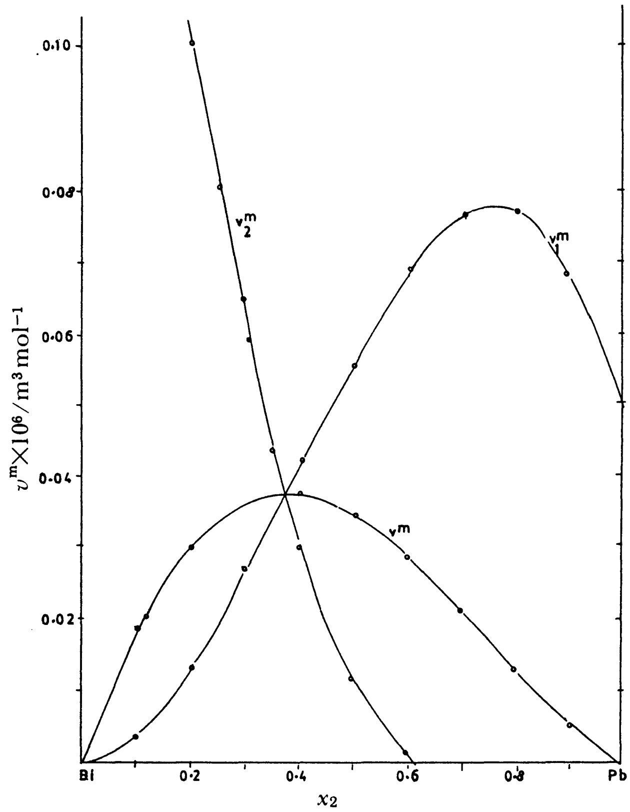

Fig. 2. Integral and partial molar volume of mixing for the liquid Bi-Pb system at 660 K.

In Table 4 are listed the values of the form function of the volume of mixing which is given by the following linear function:

$$X^{v} = 0.2298 - 0.1805\,x_2 \qquad (14)$$

As given in Table 4, the esd. ranged from 2.0×10^{-9} to 2.6×10^{-9} m^3 mol^{-1}.

References

1) I. Prigogine, A. Belleman, and V. Mathot, "The Molecular Theory of Solutions," Longmans Green, London (1957).

2) B. Predel and W. Schwermann, *Z. Metalk.*, **58**, 553 (1967).

3) F. E. Wittig and F. Z. Huber, *Phys. Chem.*, **18**, 330 (1958).

4) R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," Amer. Soc. Metals, Ohio (1973).

5) C. Wagner, "Thermodynamics of Alloys, Reading, Mass.," Addison-Wesley (1952).

6) A. Crawley, *F. Met. Trans.*, **3**, 971 (1972).

7) O. Kleppa, *J. Phys. Chem.*, **64**, 1542 (1960).