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Behavior of the Enthalpy of Mixing in the Ternary Systems Lead-Antimony-Tin, Bismuth-Lead-Tin, and Bismuth-Cadmium-Tin at 950 K. II. Theoretical Aspects

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(Received November 9, 1988)

Analysis of the experimental results which have been obtained from our studies on the ternary systems Pb-Sb-Sn, Bi-Pb-Sn, and Bi-Cd-Sn revealed a new effect: deduction of a straight line obtained by interpolation between the pairs Sb-Pb and Sb-Sn at $x_{Pb}=x_{Sn}=0.5$ from the partial enthalpy of mixing of antimony, h^{m}_{Sb}, yields a remainder quantity, ${}^{r}h^{m}_{Sb}$. The minimum of this remainder lies at the section drawing $x_{Pb}/x_{Sn}=1$. Further studies on the systems Bi-Pb-Sn and Bi-Cd-Sn indicated that the present "r-effect" is probably a general property of ternary solutions. The sign of the remainder ${}^{r}h^{m}_{i}$ is opposite to that of h^{m} of the pair of components existing vis-a-vis a third apex-component in the same ternary system. Systems of strong heteropolar character which indicate Wagner effect overlapped by III—V one could also exhibit r-effectt. Rules for the mixing behavior in binary systems are in some cases not applicable on the corresponding pairs in the ternary solutions.

The theory of liquid solution[1] failed to predict statements for the excess functions behavior in binary systems of metals and metalloids, mainly because only atomic parameters were employed to interpret the data of the excess quantities. Also the specification of the liquid state with the aid of statistical thermodynamic treatments is associated with principle difficulties and thus, these theories are only applicable to simple models. For solutions of complicated behavior of mixing, calorimetric studies seemed to be more appropriate. The results obtained from the enthalpy of mixing measurements (e.g. those by Wittig and coworkers[2–4]) proved to be useful in finding statements for the specification of the effects which could contribute in prediction of the behavior of mixing in binary solutions. These could also shed light on the factors which determine the behavior of mixing in some ternary solutions. However, studies on ternary solutions are required in order that a more definite answer to the question be provided. It is also noteworthy that in some cases, the pairs of components in a ternary system show a behavior of mixing which differs from that one observed in the binary system consisting of the same components as those in the pairs belonging to the ternary one.

In the preceeding paper,[5] the experimental results for the enthalpy of mixing in the ternary system Pb-Sb-Sn have been reported together with results for the systems Bi-Pb-Sn and Bi-Cd-Sn. The results obtained (i.e. level minima of the partial molar enthalpy of mixing of Sb and Bi) pointed out the existence of effects (e.g. the III—V effect and a present one) which contribute in determining the behavior of mixing in the ternary solutions. Our intention now is to predict statements for the behavior of mixing in relation to these effects and other possible ones. Accordingly, we report in this paper the analysis of the experimental results and theoretical approach to the ternary solutions.

Theory

The integral and partial quantities of a system of c components are given by

$$Y_i = Y - \sum_{j\neq 1} x_j \cdot \left(\frac{\partial Y}{\partial x_j}\right)_{x_k} \; ; \; j = 1,\cdots c, \tag{1}$$

where x_i is a dependent nonexplicit variable, Y, a function of all $x_j \neq x_i$. The subscript x_k on the partial derivative means that $x_k \neq x_j$, x_i is constant. Equation 1 is compatible to the following relation:

$$Y_i = Y + (1-x_i) \cdot \left(\frac{\partial Y}{\partial x_i}\right)_{x_j/x_k} \; ; \; i \neq 1,\cdots c, \; i \neq k, \tag{2}$$

where the subscript x_j/x_k is constant for all j, $k \neq i$. In view of Eq. 1 the partial quantity of the third component in the ternary system is given through the following polynominal function:

$$Y_3 = \sum_{k,l} a_{kl} \cdot x_1^k \, x_2^l \, (1-k-l). \tag{3}$$

Equation 3 depends on the average molar function, $\overline{Y}$, which can be expressed as a polynomial function:

$$\overline{Y} = \sum_{k,l} a_{k,l} \cdot x_1^k \, x_2^l \text{ with } \sum a_{00} = \sum_{k} a_{k0} = \sum_{l} a_{0l} = 0 \tag{4}$$

By this procedure, the partial quantities can be calculated from the integral ones. The calculation of Y_1 and Y_2 occurs as follows:

(i) The symmetrical procedure: From the coefficients a_{kl}, the coefficients b_{ij} or c_{ij} corresponding to the variation of the dependent variables x_1, x_2, and x_3, can be calculated and thus we obtain Y_1 and Y_2.

(ii) We can keep x_1 and x_2 as independent variables to determine Y_1 and Y_2 from Y (x_1, x_2). This is only possible when the coefficients a_{kl} are known. Applying this procedure, we obtain

$$Y_1 = \sum_{k,l} a_{kl} \, x_1^k \, x_2^l \, (1-k-l) + a_k x_1^{k-1} \, x_2^l \, k, \tag{5}$$

$$Y_2=\sum_{k,l} a_{kl}\, x_1^k\, x_2^l\,(1-k-l)+a_k\, x_1^k\, x_2^{l-1} l, \tag{6}$$

$$Y_3=\sum_{k,l} a_{kl}\, x_1^k \cdot x_2^l\,(1-k-l). \tag{7}$$

The excess quantity of the enthalpy of mixing is given through the following polynomial function:

$$Y^e=Y^e(x_i,\, x_j)=\sum_{k,l} a_{kl}\, x_i^k\, x_j^l, \tag{8}$$

where i, j=1,2 or 2,3 or 3,1. In this case, the following condition must be satisfied:

$$\sum a_{00}=\sum a_{k0}=\sum a_{0l}=0.$$

Since the total mole fraction of the three components in the ternary system must equal 1, ($x_1+x_2+x_3=1$), the excess quantities can be expressed in three different pairs of mole fraction. Substitution of the dependent mole fraction occurs as follows:

$$\begin{aligned} Y^e=Y^e(x_1,\, x_2)&=\sum_{k,l} a_{kl}\, x_1^k\, x_2^l=\sum_{k,l} a_{kl}\cdot x_1^k(1-x_1-x_3)^l \\ &=Y^e(x_1,\, x_3)=\sum_{i,j} b_{ij}\, x_3^i\, x_1^j. \end{aligned} \tag{9}$$

The calculation of the coefficient b_{ij} occurs from those a_{kl}.

Discussion

From the study[2-4] on binary systems, it was possible to derive appropriate expressions which relate the position of the components in the periodic table to the excess function, Y^e. Accordingly, statements for the expected trends and properties of the excess quantities have been predicted in some noninvestigated systems. In views of these investigations and the results from our studies on a series of ternary systems, we have obtained further conclusions concerning the behavior of the enthalpy of mixing. These results will be discussed here together with those obtained from the present study on the system Pb-Sb-Sn.[5]

In the system Bi-Cd-Sn,[5] the partial molar enthalpies of mixing of bismuth and cadmium, h^m_{Bi}, h^m_{Cd}, showed striking level minima. It was observed that the level minimum of h^m_{Cd} and the bend joined to this minimum disappear rapidly when the mole fraction of Sn increases. At the same time, the bend of h^m_{Bi} becomes larger. Consequently, the partial enthalpy of mixing of Bi takes negative values. This was a somewhat surprising observation since h^m_{Bi} in the pair Bi-Cd showed always positive trends. This behavior could not have been caused by a Wagner effect,[6] since the trend of h^m_{Bi} curve differs from that one belonging to the Wagner effect.[6] It was therefore presumed that a cluster formation (caused by covalent bonds) exists. Indeed, it was not possible to derive a strict concentration interval from which conclusions for stoichiometric relations and electronic arrangements may be obtained. We can therefore suggest a valence electron concentration (C_{ve}) equal 3 for the pair Cd-Sn in the ternary system Bi-Cd-Sn. To check the justness of these presumptions we have been studying the system Bi-Pb-Sn. The partial molar enthalpy of mixing of bismuth showed a level minimum in the region lying between the section drawings $x_{Sn}=0$ and $x_{Pb}/x_{Sn}=6/4$. Also in this system the C_{ve} of the value 3 was presumed for the pair Pb-Sn.

Since the origin of the minima observed is presumed to be caused by the combination of an element (of 5 valence electrons) with comparable pairs of elements belonging to group IIIa and having the same Cve as that of the element, it is expected that the system Cd-Sb-Sn shows similar behavior. However, the study of this system is problematic (high vapor pressure of Cd at the melting point of antimony). The system Sb-Sn-Zn shows in the pair Sb-Zn a striking strong Wagner effect. This would overlap the covalent III—V effect so that no further conclusions from this system could be obtained.

The partial molar enthalpy of mixing of antimony, h^m_{SB}, in the system Pb-Sb-Sn goes through a minimum between the quasi-binary section drawings $x_{Sn}=0$ and $x_{Sn}/x_{Pb}=6/4$. This occurs due to the transfer of electrons from antimony in such a way that the C_{ve} reaches the value of 3 at the tin side. The same behavior could be expected for the system Bi-Pb-Sn where the delivery of electrons occurs by bismuth to yield a C_{ve} of 3 at the lead side. The correct-

Table 1. ζ-Function of Antimony at Quasi-Binary Section Drawings in the System Pb-Sb-Sn Beginning from the Apex Sb in kJ mol^{-1} at 950 K

	Section drawing:										
x_{Sb}	Sn-Pb	1	2	3	4	5	6	7	8	9	Pb-Sb
0.0	−5.50	−4.90	−4.42	−3.98	−3.66	−3.16	−2.71	−2.16	−1.46	−0.66	−0.04
0.1	−5.49	−5.56	−5.58	−5.46	−5.21	−5.21	−4.29	−3.58	−2.67	−1.52	−0.26
0.2	−5.64	−5.96	−6.11	−6.04	−5.77	−5.77	−4.69	−3.90	−2.92	−1.72	−0.31
0.3	−5.72	−6.04	−6.14	−6.00	−5.65	−5.12	−4.44	−3.63	−2.69	−1.58	−0.29
0.4	−5.57	−5.79	−5.79	−5.57	−5.16	−4.60	−3.92	−3.15	−2.29	−1.33	−0.24
0.5	−5.13	−5.23	−5.15	−4.90	−4.50	−3.98	−3.36	−2.67	−1.92	−1.10	−0.17
0.6	−4.40	−4.43	−4.33	−4.12	−3.97	−3.37	−2.86	−2.28	−1.63	−0.89	−0.04
0.7	−3.48	−3.47	−3.40	−3.26	−3.05	−2.75	−2.37	−1.90	−1.32	−0.61	+0.24
0.8	−2.55	−2.48	−2.42	−2.33	−2.19	−1.98	−1.69	−1.29	−0.76	−0.06	+0.82
0.9	−1.86	−1.64	−1.44	−1.25	−1.04	−0.80	−0.48	−0.08	−0.43	+1.07	+1.87

ness of the above cited view will be quantitatively checked through testing the behavior of the ζ-function[7] which in given by

$$\xi = \frac{y_i}{(1-x_i)^2}\,, \tag{10}$$

where y_i is the partial molar quantity of the enthalpy of mixing ($h^{\mathrm{m}}_{\mathrm{Sb}}$ or $h^{\mathrm{m}}_{\mathrm{Bi}}$) and x_i the mole fraction of the component Sb or Bi.

Using the data for $h^{\mathrm{m}}_{\mathrm{Sb}}$ in the system Pb-Sb-Sn,[5] we obtain values for ζ as illustrated in Table 1. From this table, it is evident that the minimum of ζ lies at side of the pair at which $h^{\mathrm{m}}_{\mathrm{Sb}}$ takes the more negative value. This is the pair Sn-Sb where the C_{ve} reaches its maximum at the tin side.

The level form of the minima of the enthalpy of mixing of components (belonging to group Va in the periodic table of elements) at the quasi-binary section drawings x_{Bi}=const. and x_{Sb}=const., was presumed to be related to a convalent III—V effect. In fact, the relation between the form of the minima and the enthalpies of mixing of the pairs of components in ternary systems depends on other effect as observed in the present study. This effect may be explained as follows:

Deduction of a straight line (interpolated between the pairs Sb-Pb and Sb-Sn at $x_{\mathrm{Pb}}=x_{\mathrm{Sn}}=0.5$) from the partial enthalpy of mixing of antimony, $h^{\mathrm{m}}_{\mathrm{Sb}}$, yields a remainder quantity: ${}^{\mathrm{r}}h^{\mathrm{m}}_{\mathrm{Sb}}$. The minimum of ${}^{\mathrm{r}}h^{\mathrm{m}}_{\mathrm{Sb}}$ lies nearly at the section drawing $x_{\mathrm{Pb}}/x_{\mathrm{Sn}}=1$ (Fig. 1). The same effect (indicated here as r-effect) is expected to be observed in the system Bi-Sb-Sn where the minimum of ${}^{\mathrm{r}}h^{\mathrm{m}}_{\mathrm{Bi}}$ lies at the section drawing $x_{\mathrm{Sb}}/x_{\mathrm{Sn}}=1$. In both cases, the "r-effect" is probably overlapped by other properties of pairs of components in the ternary systems.

It is possible that the r-effect is a general property of ternary solutions. The properties of ternary solutions are of two origins:

Characteristic effects which have a relevant physical meaning or other ones of trivial nature e.g. the Gibbs-Duhem relation for partial quantities. On the other hand, these properties may be overlapped by a somewhat stronger effect which depends on the type of the ternary system e.g. the expected stronger effect resulting from the substitution of Sn by Zn in the system Pb-Sb-Sn. Such a substitution leads to more heteropolar character and consequently to a Wagner effect. In such cases it would be easy to find a correlation between the position of the component in the periodic table of elements and the Wagner effect.

In order to prove that the above described "r-effect" is not a property of all planes (belonging to the pairs in the ternary system) where these planes satisfy the Gibbs-Duhem relation, the following plane will be discussed:

$$h^{\mathrm{m}} = 1 - x_3 - (1-x_3)^2 + \frac{x_1\,x_2}{(1-x_3)}\,, \tag{i}$$

where x_1, x_2, and x_3 are the mole fractions of Sb, Pb, and Sn, respectively. This plane has the pair (1,2) and satisfies the Gibbs-Duhem relation.

For $x_3=0$, we have $h^{\mathrm{m}}(1,2)=x_1\,x_2$, and

$$h^{\mathrm{m}}_3 = h^{\mathrm{m}} - (x_3-1)\cdot\left(\frac{\partial h^{\mathrm{m}}}{\partial x_3}\right)_{x_1/x_2} = (1-x_3)^2\,.$$

For the section drawing x_3=const., h^{m}_3 is also constant. Despite the existence of the positive pair (1,2), h^{m}_3 is without ${}^{\mathrm{r}}h^{\mathrm{m}}_3$. This means that the plane (i) does not indicate r-effect. With this evidence one may conclude that, ${}^{\mathrm{r}}h^{\mathrm{m}}_3$, with an opposite sign to that one of the enthalpy of mixing corresponding to the pair which exists at the opposite side to the third component in the same ternary system, is not a trivial property which can be derived from the Gibbs-Duhem relation.

To decide that the above described ${}^{\mathrm{r}}h^{\mathrm{m}}_{x_i}$ is a general property of other ternary systems and to show how this effect takes place, we discuss the behavior of the

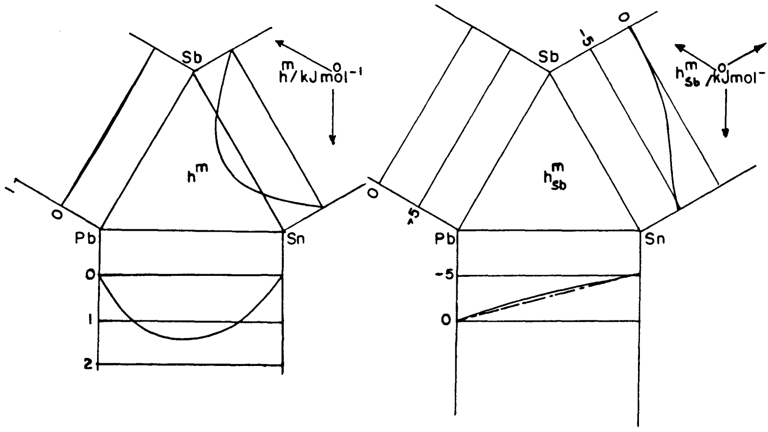

Fig. 1. The molar enthalpy of mixing, h^{m}, the partial one of antimony, $h^{\mathrm{m}}_{\mathrm{Sb}}$, at the quasi-binary section drawings Sb-Pb and Sb-Sn in the system Pb-Sb-Sn and the "r-effect."

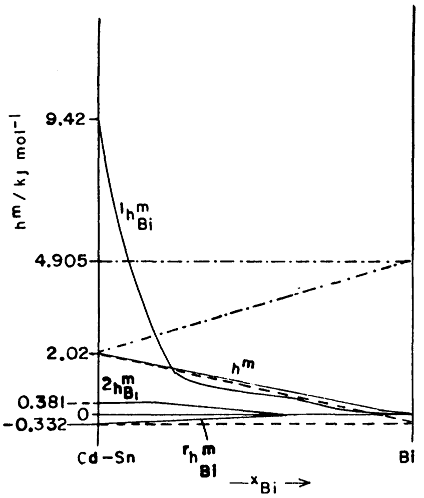

Fig. 2. Representation of the "r-effect" and estimated ${}^{r}h^{m}_{\mathrm{Bi}}$ in the system Bi-Cd-Sn.

enthalpy of mixing of bismuth, h^{m}_{Bi}, using our data for the system Bi-Cd-Sn.[5] The partial molar enthalpy of bismuth is given by

$$h^{m}_{\mathrm{Bi}} = h^{m} + (1-x_3)\cdot\left(\frac{\partial h^{m}}{\partial x_3}\right)_{x_1/x_2}, \qquad (11)$$

where x_1, x_2, and x_3 are the mole fractions of Bi, Cd, and Sn, respectively. Figure 2 shows the trends of the partial molar enthalpies of mixing, ${}^{2}h^{m}_{\mathrm{Bi}}$ at Sn-Bi and ${}^{1}h^{m}_{\mathrm{Bi}}$ at Cd-Bi together with the curve of the molar enthalpy of mixing along the quasi-binary section drawing $x_{\mathrm{Cd}}/x_{\mathrm{Sn}}=1$ in the ternary system Bi-Cd-Sn.

The partial enthalpies of mixing of bismuth at the spices $x_{\mathrm{Cd}}=1$ and $x_{\mathrm{Sn}}=1$ are 9.42 and 0.39 kJ mol^{-1}, respectively. From linear interpolation, we can obtain for $x_{\mathrm{Cd}}=x_{\mathrm{Sn}}=0.5$, the value of 4.91 kJ mol^{-1}. The molar enthalpy of mixing in the system Bi-Cd-Sn at $x_{\mathrm{Cd}}=x_{\mathrm{Sn}}=0.5$ is 2.02 kJ mol^{-1}. With reference to Eq. 11, the partial enthalpy of mixing of bismuth at this point can reach the average value 4.91 kJ mol^{-1} only when the molar enthalpy of mixing, h^{m}, starting from 2.88 kJ mol^{-1}, increases. With linear continuous increase where the drop in the value of h^{m} is, according to $h^{m}=a(1-x_{\mathrm{Bi}})$, proportional to x_{Bi}, the partial molar enthalpy of mixing of bismuth h^{m}_{Bi} takes, along the whole quasi-binary section drawing $x_{\mathrm{Cd}}/x_{\mathrm{Sn}}=1$, the value of zero. When h^{m} without a turning point goes below this straight line, the partial enthalpy of mixing of bismuth, h^{m}_{Bi}, becomes along the whole quasi-binary section drawing negative. This means that the sign of ${}^{r}h^{m}_{\mathrm{Bi}}$ is opposite to that one of the pair which exists at the opposite side of bismuth in the system Bi-Cd-Sn.

On the basis of the above given discussion, we expect that for ternary systems such as Bi-Sb-M (M=metal), in which Bi or Sb exists vis-a-vis a pair with negative enthalpy of mixing, the h^{m}_{Bi} in the pair Sb-M and h^{m}_{Sb} in that one Bi-M should have positive ${}^{r}h^{m}_{\mathrm{Bi}}$ and ${}^{r}h^{m}_{\mathrm{Sb}}$, respectively.

Conclusion

The r-effect is probably a general property of ternary solutions. The level minima of the partial quantities of the enthalpy of mixing in ternary solutions are attributed to the r-effect. Systems of strong heteropolar character which indicate Wagner effect overlapped by III—V effect exhibit also r-effect. Rules for the mixing behavior in binary systems are in some cases not applicable on the corresponding pairs in the ternary solutions.

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