Behavior of the Enthalpy of Formation in the Tin-Antimony System

Walid Ahmad BADAWI*,† and Ali Esa EID
Department of Chemistry, Faculty of Science, Al-Fateh University, Tripoli, Libya
†P. O. Box 13539, Tripoli, Libya
(Received May 9, 1986)

Calorimetric studies on the behavior of the enthalpy of formation in the tin-antimony system have been carried out at five different compositions (43.3—55 at -% Sb). The enthalpy of dissolution has been determined at 796.15 and 768.15 K. The enthalpy of formation is negative and takes a maximum value (2.906±0.002 kJ mol^{-1}) at 298.15 K for 50 at-% Sb. The molar enthalpy of mixing is more positive than that of formation. On comparing with partial molar enthalpy of mixing, the partial molar enthalpy of formation of tin is shifted to more negative values, while that of antimony to more positive values.

In recent years, the study of thermodynamic properties of binary systems of metals has attracted much interest. One such system, namely tin-antimony has been studied by some researchers eg. phase diagram by Predel and Schwermann[1] and heat of mixing by Wittig and Gehring[2] and other authors.[3] Also in this laboratory, work has been carried out in order to study the behavior of the enthalpy of formation of the β'-phase in the tin-antimony system[4] and to obtain the ratio of the enthalpies of formation to those of mixing. This would facilitate interpolation of the behavior of the enthalpy of formation at positions having indefinite structures.

Experimental

Sample. The metals used were of extra purity grade. These were procured from Riedel de Haen Co. The alloys samples were produced in cylindrical forms (ϕ=4.5—5mm; h=12—16 mm) by means of a melting device (Fig. 1). By this melting device, while the clean liquid metal flows down into the lower tube of quartz, the oxide layer remains apart in the first one. The mixture of tin and antimony was stirred mechanically with a stirrer made of ceramic for 30 min at 873 K. In order to reduce the effect of oxidation, argon gas was used as a protector during the melting process. The samples were tempered for 6 h at 673 K, 6 h at 623 K, and 192 h at 483 K.

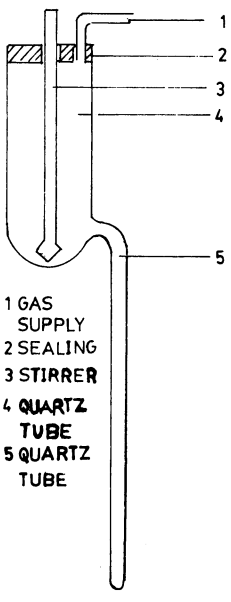


Fig. 1. Melting device.

Table 1. Lattice Constant of the β'-Phase in Sn Sb System (Found/Ref.)

x_{Sb}	a in Å (Found)	a in Å	(Ref.)
0.433	6.118	6.133	6
0.450	6.103	[6.136]	7
0.500	6.116	[6.120]	8
0.525	6.100	[6.136]	8
0.550	6.118	[6.134]	1

The values between the brackets were calculated from KX. The reported a values for 50 at-% Sb are different. They fluctuate between 6.104 and 6.138 Å.

Calorimeter. The calorimeter used was a slightly modified version of the type described by Wittig and Gehring.[2]

Theory and Procedure

The enthalpy of dissolution of solid antimony in liquid tin can be determined at the temperature T_1 through the equations

$$-(1-x_2)\cdot \mathrm{Sn}(1, T_1)-x_2\cdot \mathrm{Sb}(s, T_1)+\mathrm{Sn}_{1-x_2}\mathrm{Sb}_{x_2}(1, T_1)=0, \quad (1)$$

$$h^s=-(1-x_2)\cdot h_1(T_1)-x_2\cdot h_2(T_1)+h_3(T_1), \quad (2)$$

where, h^s is the enthalpy of dissolution of solid antimony in liquid tin, h_3 the enthalpy of the alloy at the mole fraction of antimony x_2.

The enthalpy of dissolution has been determined at 796.15 and 768.15 K.

The enthalpy of formation is the special form of the enthalpy of reaction evolved by the formation of the substance from the elements. In the case of the tin-antimony alloy, the formation reaction is

$$-(1-x_2)\cdot \mathrm{Sn}(s, T_0)-x_2\cdot \mathrm{Sb}(s, T_0)+\mathrm{Sn}_{1-x_2}\mathrm{Sb}_{x_2}(s, T_0)=0, \quad (3)$$

where, T_0 is the initial temperature.

The enthalpy of formation is then

$$h^F=-(1-x_2)\cdot h_1(T_0)-x_2\cdot h_2(T_0)+h_3(T_0). \quad (4)$$

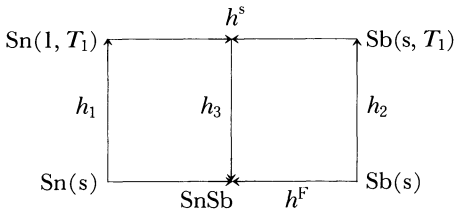
The indices 1, 2, and 3 indicate tin, antimony, and the alloy, respectively.

Subtraction of Eq. 4 from Eq. 2 yields

$$h^s-h^F=-(1-x_2)\cdot[h_1(T_1)-h_1(T_o)]-x_2[h_2(T_1)-h_2(T_o)]+[h_3(T_1)-h_3(T_o)]. \quad (5)$$

The term $h_3(T_1)-h_3(T_o)$ which appears in Eq. 5 is the enthalpy difference of the alloy; this was measured between 298.15 and 768.15 K; between 483.15 and 796.15 K. The enthalpy differences $h_1(T_1)-h_1(T_o)$ and $h_2(T_1)-h_2(T_o)$ are measured accurately (s. Table 3).

This procedure can be illustrated with reference to the following scheme:



The non-measurable process of the enthalpy of formation at T_o will be substituted by (1) heating of tin and antimony at T_1, (2) measurement of the enthalpy difference of the single miscible phase between T_o and T_1 and (3) measurement of the enthalpy of dissolution at T_1. Employing the present procedure, the enthalpy of formation has been experimentally determined at five different compositions. From the obtained values of the enthalpy of formation an appropriate polynomial function is given (Eqs. 6 and 7).

Results and Discussion

(i) Lattice Constants. Results of the lattice constant determinations are presented in Table 1 together with the values reported by other authors.[1,6-8] The quoted lattice constants of the β'-Sn Sb vary regularly with the composition. The a value for 50 at-% Sb is in agreement with that reported by Osawa,[8] while those for other compositions differ 0.245 to 0.59% from earlier ones.

(ii) Enthalpy of Dissolution. Table 2 represents values of the enthalpy of dissolution of solid antimony in liquid tin at 768.15 and 796.15 K. The results have been least squares fitted by a polynomial expression, with a standard deviation of 0.4% for a single measurement. The enthalpy of dissolution varies regularly with the composition as the associated lattice constant data do.

(iii) Enthalpies. Table 3 represents values of $h_1(T)-h_1$(298.15 K); $h_1(T)-h_1$(483.15 K) and $h_2(T)-h_2$(298.15 K); $h_2(T)-h_2$(483.15 K) as determined by the present study. The average error of the individual measurement was found to be 0.32%, while the deviation of the single measurement of the earlier reported data (s. Ref. 9) was estimated to be 1—2%.

Values of $h°$(768.15 K)$-h°$(298.15 K) and $h°$(796.15 K)$-h°$(483.15 K) of the alloys are collected in Table 4 at five compositions. The deviation is 0.3% for a single measurement.

(iv) Integral and Partial Molar Enthalpy of Formation. The integral and partial molar enthalpies of formation at 298.15 and 483.15 K are illustrated in Table 5 for five different compositions. The average error of the individual measurement was found to be 0.41% for T=298.15 K and 0.3% for T=483.15 K.

Using the data in Table 5, it was possible to derive empirically, equations which represent the shapes of the curves drawn in Figs. 2 and 3 as follows:

Table 2. Experimentally Determined Enthalpy of Dissolution of Solid Antimony in Liquid Tin in J mol^{-1}
M(Sn)=118.7 g mol^{-1}; M(Sb)=121.76 g mol^{-1}

x_2	0.433	0.450	0.500	0.525	0.550
h^s(796.15 K)	7382	7729	8753	9281	9821
h^s(768.15 K)	7212	7552	8549	9113	9590

Table 4. Enthalpy Difference of the Alloys in J mol^{-1}
M(Sn)=118.7 g mol^{-1}; M(Sb)=121.76 g mol^{-1}

x_{Sb}	$h°$(796.15)$-h°$(483.15 K)	$h°$(768.15)$-h°$(298.15 K)
0.433	23790	28067
0.450	23796	28091
0.500	23822	28057
0.525	23903	28066
0.550	23816	28040

Table 3. Experimentally Determined Enthalpy Differences of Tin and Antimony
M(Sn)=118.7 g mol^{-1}; M(Sb)=121.76 g mol^{-1}

T/K	$h_1(T)-h_1$(298.15 K)	$h_1(T)-h_1$(483.15 K)	$h_2(T)-h_2$(298.15 K)	$h_2(T)-h_2$(483.15 K)
	J mol^{-1}	J mol^{-1}	J mol^{-1}	J mol^{-1}
298.15	0	—	0	—
400	2850	—	2612	—
500	5820	458	5239	410
505.11(s)	5985	623	—	—
505.11(l)	13010	7648	—	—
600	15755	10393	7912	3083
700	18617	13255	10670	5841
768.15	20550	15188	12654	7825
796.15	21354	15275	13432	8723
800	21462	16100	13541	8842
900	24309	18947	16552	11723

Table 5. Enthalpy of Formation of the β'-Phase in the Tin-Antimony System in J mol^{-1}, (Calcd) Found

x_{Sb}	T=298.15 K			T=483.15 K		
	$-h^F$	$-h_1^F$	$+h_2^F$	$-h^F$	$-h_1^F$	$+h_2^F$
0.433	(3736) 3724	8540	2625	(3960) 3970	9043	2698
0.450	(3541) 3542	8851	2950	(3755) 3741	9316	3042
0.500	(2908) 2906	9664	3849	(3092) 3070	10178	3995
0.525	(2559) 2549	10103	4266	(2726) 2787	10643	4437
0.550	(2189) 2200	10563	4662	(2338) 2324	11130	4856

$$h^F=-5.387-3.606x_2+17.12x_2^2;\ T=298.15\ \text{K}, \quad (6)$$

$$h^F=-5.642-3.970x_2+18.14x_2^2;\ T=483.15\ \text{K}. \quad (7)$$

It is apparent that the enthalpy of formation depends insignificantly on the temperature (Figs. 2 and 3).

The data in Table 5 clearly indicate that the enthalpy of formation increased with the increase of antimony mole fraction. This behavior is expected due to the charging of the Brillouin zones.

For a heteropolar behavior, a minimum of the enthalpy of formation is expected to appear at 40 at-% Sb. This minimum could not be observed in the normally experimental values. This is due to the fact that the deformation energy constrains the minimum of the enthalpy of formation to shift from a stoichiometric

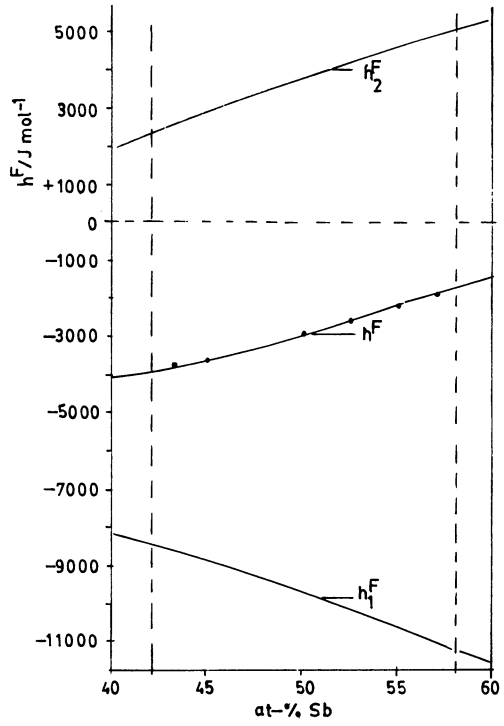


Fig. 2. Integral and partial enthalpy of formation in the tin-antimony system at 298.15 K.

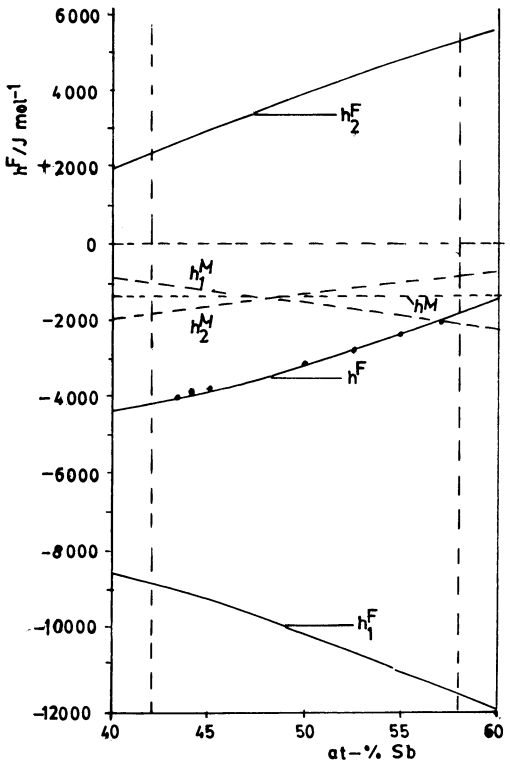


Fig. 3. Integral and partial enthalpy of formation in the tin-antimony system at 483.15 K.

composition to other mole fraction of antimony.

The partial molar enthalpies of formation of tin and antimony are given by

$$h_1^F=h^F-x_2\cdot(\partial h^F/\partial x_2)_{T,p}, \quad (8)$$

and

$$h_2^F=h^F-(x_2-1)\cdot(\partial h^F/\partial x_2)_{T,p}. \quad (9)$$

Using Eqs. 6, 7, 8, and 9, we have

$$h_1^F=-5.385-17.12\,x_2^2 \quad h_2^F=+8.13-17.12\,(x_2-1)^2 \quad T=298.15\ \text{K}, \quad (10)$$

$$h_1^F=-5.642-18.14\,x_2^2 \quad h_2^F=+8.527-18.14(x_2-1)^2 \quad T=483.15\ \text{K}. \quad (11)$$

The curve in Fig. 3 shows that the partial molar enthalpy of antimony is positive and shifts to more positive values at higher composition. This is due to the insertion of the larger antimony atom in the structure of Sn Sb which becomes instable at higher mole fraction of antimony. The structure exhibits a higher tension resulting from the deformation work which is associated with the insertion of the antimony atom in th structure.

The partial molar enthalpy of tin is negative and becomes more negative at higher composition.

A hypothetical illustration of this behavior is probably that a poor fraction of tin p-electrons builds a weak bond with antimony ions. At higher mole fraction of antimony, the equilibrium shifts for the benefit of the delivery of further electrons on antimony.

On the basis of the above discussion, we come to the

following conclusion:

(1) The average molar enthalpy of mixing is more positive than that of formation.

(2) On comparing with partial molar enthalpy of mixing, the partial molar enthalpy of formation of tin is shifted to more negative values, while that of antimony to more positive values.

References

1) B. Predel and W. Schwermann, *J. Inst. Metals*, **99**, 169 (1971).

2) F. E. Wittig and E. Z. f. Gehring, *Naturforshung*, **18a**, 351 (1963).

3) A. Yazawa, T. Kawashima, K. Itagaki, *Nippon Kinzoku Gakkaishi*, **32**, 1288 (1968).

4) B. C. Ellwood, "The Equilibrium Diagram of the System Tin-Antimony," J. Wiley, London (1956) 1/6.

5) J. Czochralski and E. Przyjemski, *Wiadomosci Inst. Metallurg. Metaloznawstwa*, **3**, 113 (1936).

6) C. A. McKay, *J. Appl. Crystallogr.*, **2**, 295/7 (1969).

7) E. G. Bowen and W. Morris-Jones, *Philos. Mag.*, 7/12 (1931) 441/62, 446.

8) A. Osawa, *Nature*, 2124 (1929) 14.

9) Hultgren et al., "Selected Values of the Thermodynamic Properties of Metals and Alloys," American Society for Metals, Metals Park, Ohio (1973).