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A Calorimetric Study on the β' Phase in the System Tin-Antimony. Enthalpies of Mixing and Formation

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Calorimetric studies on the behavior of the enthalpy of formation at 573 K in the system tin-antimony have been carried out at the compositions 44, 50, 57 at-% Sb using a presently constructed calorimeter. The enthalpy of mixing at 943 K has been determined in the whole range of composition. The relation of the behavior of mixing to that of formation is found as predicted earlier. The enthalpy of formation displays a pronounced temperature dependence above 623 K. The thermodynamic properties of the alloy SnSb at the three compositions exclude a transformation from β to β' phase around 600 K. Also estimated entropy terms indicate the absence of such a transformation. Earlier reported additional β phase in the system Sn–Sb seemed therefore not to be present.

In our previous studies[1,2] on the enthalpy of formation in the systems Bi–Sb and Sn–Sb, it was observed that the enthalpy of formation depends insignificantly on the temperature. On the other hand, Wittig and Schöffl[3] reported a pronounced temperature dependence of the heat of formation in the systems Al–Ag and Al–Zn. Such a temperature dependence was claimed to be a typical property of all metallic alloys. In order to determine the range of temperature for which this statement could be valid we have again been studying the system Sn–Sb, however, using a different procedure and a presently constructed isoperibolic calorimeter. This should also confirm the results obtained from our study[2] on the enthalpy of formation in this system and consequently test the accuracy of our calorimeter.

The phase boundaries in the system Sn–Sb have not yet been precisely predicted and diverging opinions and results exist with regard to the structures of the phases present and their transformations. Hansen and Anderko[4] rerported the existence of β and β' phases in the system Sn–Sb. According to their studies the transformation from β to β' phase should be accompanied by a change in the structure so that the β phase with a NaCl-structure exists above 598 K, while the β' phase with a distorted rhombohedral structure appears below 598 K in the region 42—58% Sb.

The present study on the system tin-antimony has been carried out in order to determine the existence of the β phase and its transformation. This would be possible by studying the thermodynamic properties of this system.

Experimental

Sample. The metals used were of extra purity grade (Riedel de Haen Co.). The preparation, treatment, and testing of the samples were all the same as reported earlier.[2]

High Temperature Diffraction Study. X-Ray (powder) photographs for samples at the compositions 58 and 50 at-% Sb were taken at 598 and 698 K (Table 1). They revealed nearly the same values for the lattice constant as those at room temperature.[2]

High Temperature Calorimetry. The calorimeter operates quasi-isothermally and represents an isoperibolic type of calorimeter. The cylindrical calorimeter of Thermax steel (Thermax 10, production No. 4742, Ger.) with a mass of 202 g is used as a sample container. The hollow space of the calorimeter is coated with a layer of aluminium oxide and its purpose was to prevent reaction of the sample with the calorimeter. The cover of the calorimeter, also coated with a layer of Al_2O_3, has three wells for the tube of the drop device, stirrer (made of ceramic) and Pt-to-(Pt+10 mass per cent Rh) thermopile. The calorimeter is suspended inside a metallic shield system of V2A steel which contains two cylindrical compensating systems of Thermax steel placed below and above the calorimeter. The lower compensating body has wells of each 3.5 mm diameter for the twelve differential thermopiles. The whole assembly is placed in a vertical tube furnace (R=41Ω). Another tube furnace (R=35Ω) is placed above the cooling system which in turn was placed at the mouth of a tube of silica glass containing the whole assembly. The purpose of the second tube furnace was to warm the sample before its final drop in the calorimeter.

The temperature difference between the calorimeter and lower compensating system are measured by means of a set of twelve differential thermopiles. These were calibrated on a standard Pt–PtRh thermopile. The accuracy obtained was found to be ±0.1 K. The thermal potential of the thermopiles is measured by means of a digital millivoltmeter (Hewlett-Packard 2401 C). The temperature drifts of the calorimeter from the lower compensating system are of negligible importance. The observed short-term fluctuation of the null-point is measured to 2×10^{-4} K min^{-1}. Excellent regulation of the temperature was obtained by means of a p-regulator.[5] The derived temperatures are judged to correspond with the IPTS-68 within 0.01 K at 500 K and 0.1 K at 1000 K. In fact the precision is considerably better, and the temperature increments are measured to 0.0003 K.

The calibration of the calorimeter occured on exactly measured enthalpy of tin sample.[3] The calibration factor is determined with an accuracy of 0.3% to an average value: ϕ=85.0±0.31 mV^{-1} min^{-1}.

The operation with this calorimeter can be explained with the aid of Table 2 and Fig. 1 which describe the process and evaluation of a measurement on alloy sample as follows: Using the quasi-isothermal procedure, the calorimeter equation of 1st order becomes

$$Q = k\cdot\int_0^n(\vartheta - \bar{\vartheta}_v)\mathrm{d}t = K\cdot A \qquad (1)$$

where Q is the heat produced in the calorimeter in J, K the constant of heat interchange in W K^{-1}, ϑ the difference between the temperature of the calorimeter and that of the thermostat (compensating system) in the main period which represents the sum of all reads in the main period, and $\bar{\vartheta}_v$ the average value of all reads in the null-point periods: $\bar{\vartheta}_v=(\vartheta_v+\vartheta_n)/n$. A refers to the area under the curve as shown in Fig. 1 and t to the time in second. The determination of A and calculation of the heat content of an alloy sample are illustrated in Table 2: Subtraction of the average value of $\bar{\vartheta}_v$ and ϑ_n from all reads in the main period yields a reduced quantity which represents the deviations in the temperature of the calorimeter from the null-point in the pre- and post-period. The reduced quantity will be integrated according to the trapezoidal rule: The sum of the first and last reads in the main period will be devided by 2. Addition of this result to the sum of all reads between the first and last one gives the area A.

Table 1. Lattice Constants of the Alloy SnSb

T/K	x_{Sb}	a/Å
598	0.500	6.120
	0.580	6.116
698	0.500	6.117
	0.580	6.118

Procedure of Enthalpy Measurement. The enthalpy of mixing of liquid tin and liquid antimony can be determined

Table 2. The Process and Evaluation of a Measurement on a Sample of the Tin-Antimony Alloy

Pre-period	Main-period	Post-period
3.188 mV min	3.307 264	3.186
3.187	3.612 254	3.187
3.187	3.564 254	3.187
3.187	3.522 236	3.187
3.187	3.488 229	3.187
3.187	3.456 222	3.187
3.187	3.426 215	3.186
3.187	3.400 209	3.187
3.186	3.376 204	3.187
3.187	3.355 200	3.187
	3.336 197	
	3.318 194	
	3.303 191	
	3.289 190	
	3.276 189	
ϑ_v=187 mV min	ϑ_n=188.6 mV min	$A=(A_1+A_2)/2$=3.66 mV min
$A_1=\sum(\vartheta_i-3)-t\cdot\sum(\vartheta_v-3)$=3.657 mV min		$H=A\cdot\varphi$=311.7 J
$A_2=\sum(\vartheta_i-3)-t\cdot\sum(\vartheta_n-3)$=3.657 mV min		h=28076 J mol^{-1}

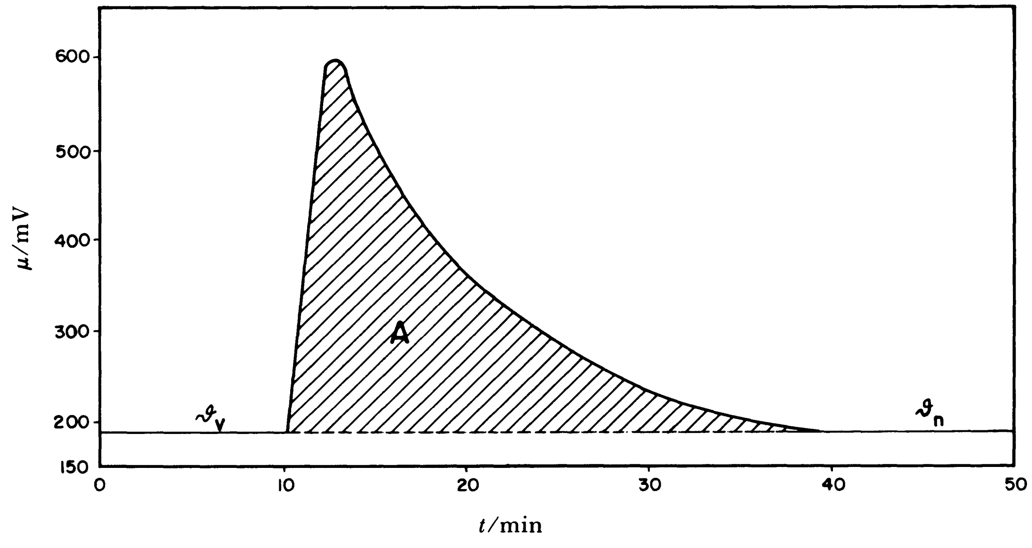


Fig. 1. Plot of the thermal potential μ versus the time t for a measurement on alloy sample using the present calorimeter.

at the temperature T through the equations

$$-(1-x_2)\cdot \mathrm{Sn}(l,T) - x_2\mathrm{Sb}(l,T) + \mathrm{Sn}_{1-x_2}\mathrm{Sb}_{x_2}(l,T) = 0 \tag{2}$$

$$h^{\mathrm{M}} = -(1-x_2)\cdot h_1(T) - x_2 h_2(T) + h_3(T) \tag{3}$$

where h^{M} is the enthalpy of mixing of liquid tin and liquid antimony, h_3 the enthalpy of the alloy at the mole fraction of antimony x_2.

The enthalpy of mixing has been determined at 943 K in the whole range of composition (Table 3).

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

$$-(1-x_2)\cdot \mathrm{Sn}(\mathrm{s},T_0) - x_2\cdot \mathrm{Sb}(\mathrm{s},T_0) + \mathrm{Sn}_{1-x_2}\mathrm{Sb}_{x_2}(\mathrm{s},T_0) = 0. \tag{4}$$

The enthalpy of formation is then

$$h^{\mathrm{F}} = -(1-x_2)\cdot h_1(T_0) - x_2\cdot h_2(T_0) + h_3(T_0) \tag{5}$$

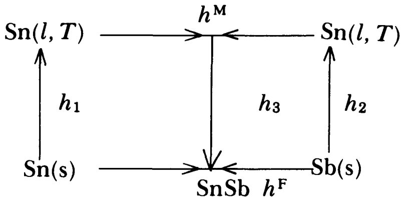
Indices 1, 2, and 3 refer to tin, antimony, and the alloy, respectively.

Subtraction of Eq. 5 from Eq. 3, yields

$$h^{\mathrm{M}} - h^{\mathrm{F}} = -(1-x_2)[h_1(T) - h_1(T_0)] - x_2[h_2(T) - h_2(T_0)] + [h_3(T) - h_3(T_0)] = {}^{e}h(T) - {}^{e}h(T_0) \tag{6}$$

where ${}^{e}h(T)-{}^{e}h(T_0)$ is the difference in the excess enthalpy of the alloy. The term $h_3(T)-h_3(T_0)$ is the enthalpy difference of the alloy; this was measured at even temperature interval of 10 K in the range 298.15 K to 923 K and tabulated together with the difference of the excess enthalpy at even temperature interval of 50 K in the same range of temperature. The enthalpy difference of tin and antimony are measured accurately (Table 4). All these heat contents have been measured using the present technique: The solid sample can be tempered at any temperature using a pre-furnace (see the description of the calorimeter) before the drop in a liquid phase of the same substance and composition existing inside the calorimeter. In this case the pre-dissolving of the sample is not required since the melting occurs in a liquid phase having the same composition as that of the sample so that the complications of the solution-calorimetry can be avoided. This also enables us to obtain the enthalpy difference between the solid and liquid phases.

The procedure for measurement of the enthalpy of formation (refer to Eq. 6) can be illustrated with reference to the following schema:



The non-measurable process of the enthalpy of formation will be substituted by (1) heating of tin and antimony at T, (2) measurement of the enthalpy of mixing at T, and (3) measurement of the enthalpy difference of the single miscible phase between T_0 and T. The value of h^{F} has been determined at three compositions (Table 7) employing the present procedure.

Results and Discussion

(i) Lattice Constant. Results of the lattice constant determinations at 598 and 698 K for the compositions 50 and 58 at-% Sb in the system Sn–Sb are presented in Table 1. They compare surprisingly well with those at room temperature.[2] These results are compatible to those expected for a β' phase with distorted rhombohedral structure.[4] This gives the first signal for the non-existence of further β phase claimed to be present in the phase diagram of the system SnSb.[4]

(ii) Enthalpy of Mixing. In Table 3 are listed the values of the enthalpy of mixing as determined in the present study. The results have been least squares fitted by a polynomial expression with a standard deviation of 0.3% for a single measurement. The present value of h^{M} is in good agreement with that by Hultgren et al.[6] and Wittig.[7] Also the result by Kleppa[8] who gives an accuracy of 1% for his measurements is in reasonable agreement with the present one.

(iii) Enthalpies. Table 4 illustrates values for $h_1(T)-h_1(298.15\ \mathrm{K})$ and $h_2(T)-h_2(298.15\ \mathrm{K})$ as measured in the present study. The average error of the individual measurements was found to be 0.32%, while the deviation for a single measurement of earlier reported data[6] was estimated to be 1—2%.

Table 3. Enthalpy of Mixing in the Tin-Antimony System at 943 K in J mol^{-1}. Estimated Standard Deviations in Parenthesis

x_{Sb}	$-h^{\mathrm{M}}$	x_{Sb}	$-h^{\mathrm{M}}$
0.0	0	0.6	1310(4)
0.1	497(2)	0.7	1101(3)
0.2	788(3)	0.8	794(2)
0.3	1180(4)	0.9	419(1)
0.4	1352(4)	1.0	0
0.5	1395(4)		

Table 4. Experimentally Determined Enthalpy Differences of Tin and Antimony in J mol^{-1}. M(Sn)=118.7 g mol^{-1}; M(Sb)=121.76 g mol^{-1}

T/K	$h_1(T)-h_1(298.15\ \mathrm{K})$	$h_2(T)-h_2(298.15\ \mathrm{K})$
298.15	0	0
400	2850	2612
500	5820	5329
600	15755	7912
700	18617	10670
800	21462	13541
900	24309	16552
923	24995	37160

Table 5. Experimentally Determined Enthalpy and Excess Enthalpy Differences in the System Tin-Antimony in J mol^{-1}

	$h_3(T)-h_3(298.15\text{ K})$			$^eh(T)-{}^eh(298.15\text{ K})$		
x_2	0.44	0.50	0.57	0.44	0.50	0.57
T/K						
298.15	0	0	0	0	0	0
323	750	650	650	−12	−21	−22
373	1990	1990	1890	−12	−83	−88
423	3370	3170	3370	−59	−136	−143
473	4820	4580	4530	−141	−136	−165
523	6350	6040	5950	−4356	−3742	−3467
573	8010	7530	7240	−3569	−3586	−3335
623	12310	9100	8980	−528	−3336	−3105
673	22480	16370	12450	9850	2950	−669
723	26920	26140	24910	13513	11665	11431
773	28330	27630	27980	13619	11780	13318
823	29700	28060	29620	13701	11780	13647
873	30475	30210	30980	13771	11738	13669
923	32430	31460	32340	4684	1282	461

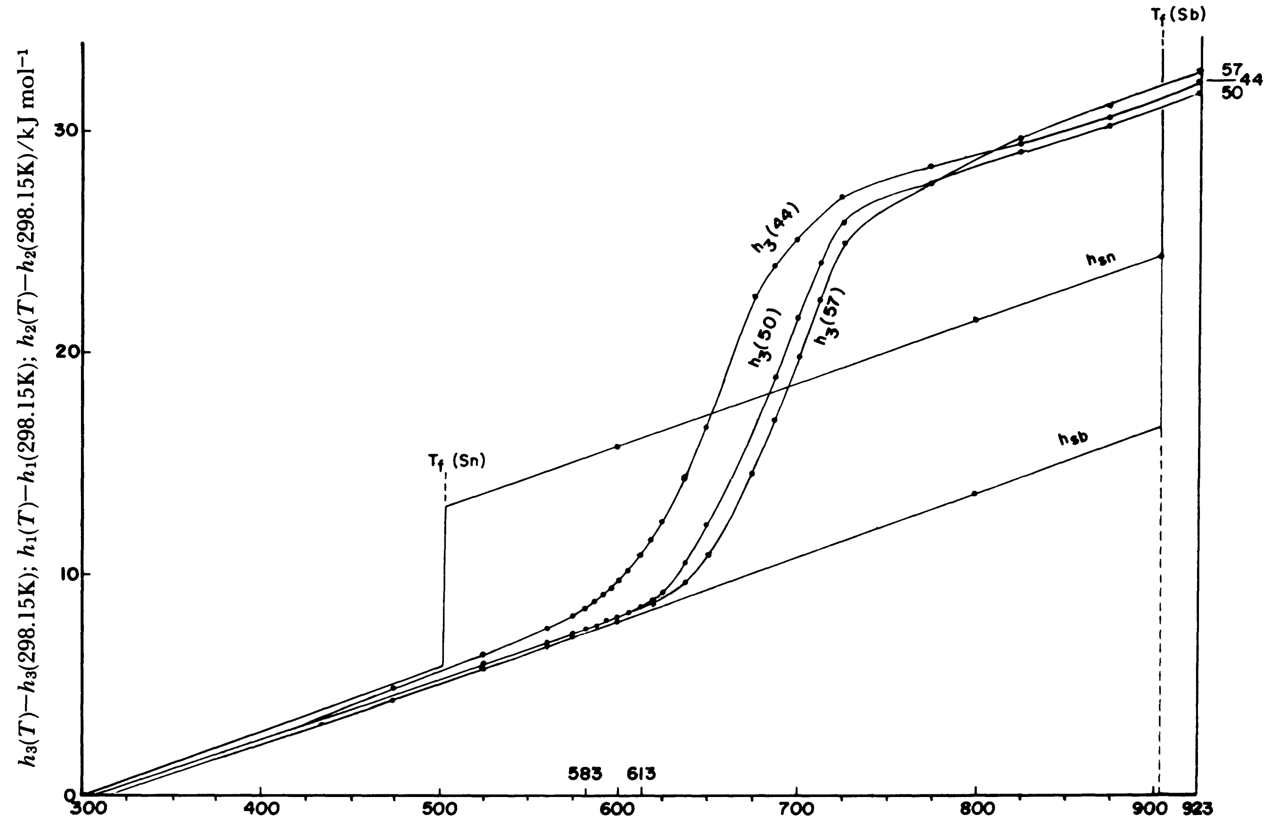


Fig. 2. Dependence of the enthalpy difference of Sn, Sb, and the alloy at the compositions 44, 50, and 57 at-% Sb on the temperature T.

In Table 5 are listed the present values of the enthalpy and excess enthalpy differences of the alloy SnSb in the region 298.15 to 923 K. The estimated standard deviation is 0.35% for a single measurement. Figure 2 shows the curves of the enthalpy differences of Sn and Sb against temperature in the range 300 to 923 K together with those for the enthalpy differences of the alloy at 44, 50, and 57 at-% Sb in the same range of temperature. The values of $h_3(T)-h_3(298.15\text{ K})$ for the three compositions in the region 583 to 618 K (as a part of the whole range 298.15 to 923 K) are obtained from a separate series of experiments using the present calorimeter and Wittig's one[7] for C_p measurements. The purpose of these additional measurements was to find

Table 6. Thermodynamic Properties of the Alloy SnSb for Selected Temperature in the Range 298.15 to 923 K

	C_P			$h_3^\circ(T)-h_3^\circ(298.15\,\mathrm{K})$			$S^\circ(T)-S^\circ(298.15\,\mathrm{K})$		
	$\mathrm{J\,K^{-1}\,mol^{-1}}$			$\mathrm{J\,mol^{-1}}$			$\mathrm{J\,K^{-1}\,mol^{-1}}$		
x_2	0.44	0.50	0.57	0.44	0.50	0.57	0.44	0.50	0.57
T/K									
583	31.14	26.67	26.72	8900	7625	7610	20.88	17.88	17.91
589	31.13	26.86	26.81	9125	7850	7841	21.19	18.28	18.25
593	31.38	26.91	26.88	9225	7905	7889	21.58	18.50	18.48
595	31.49	26.98	26.91	9305	7955	7949	21.76	18.59	18.59
597	31.51	26.98	26.96	9399	8007	8001	21.88	18.73	18.73
600	31.79	26.99	26.99	9602	8075	8063	22.23	18.87	18.87
603	32.11	26.99	27.01	9805	8189	8175	22.62	19.01	19.02
606	33.08	26.99	27.03	10195	8211	8202	23.46	19.14	19.17
613	34.24	27.00	27.03	10800	8390	8377	24.77	19.46	19.48
618	35.85	27.00	27.07	11500	8750	8721	26.13	19.68	19.73

thorough trace for the trends of $h_3(T)-h_3(298.15\,\mathrm{K})$ around 600 K in order to detect any phase transformation which should occur around this temperature.[4)]

In the case of a phase transformation, the curve of h_3 should indicate an abrupt rise in a form of a sharp bent around 600 K. Since this is not observed experimentally, such a transformation can be excluded (refer to Fig. 2).

(iv) Thermodynamic Properties of the Alloy. Table 6 represents values of C_p, $h_3^\circ(T)-h_3^\circ(298.15\,\mathrm{K})$, and $S^\circ(T)-S^\circ(298.15\,\mathrm{K})$ of the alloy SnSb at the compositions 44, 50, and 57 at-% Sb for selected temperatures in the range 298.15 to 923 K. The C_p for the composition 44 at-% Sb indicates a somewhat significant increasing trend due to the partially melting of the alloy in accordance with the phase diagram of the system Sn–Sb, while C_p for 50 and 57 at-% Sb increases insignificantly with the temperature. This is due to the fact that the alloy at the last two compositions can persist until 618 K. Since C_p at 698 K dose not display an abruptly increasing trend which could point out phase transformation, the β phase seems not to be producible.

Further important evidence for the absence of a transformation from β' to β phase is obtained from the quantitative information of the entropy terms: With reference to Table 6, the increase in the entropy change between 597 and 600 K is 0.45 J K^{-1} mol^{-1} for 44 at-% Sb, and 0.04 J K^{-1} mol^{-1} for 50 and 57 at-% Sb; and that between 593 and 600 K is 0.47, 0.39, and 0.39 J K^{-1} mol^{-1} for 44, 50, and 57 at-% Sb, respectively. Also the increase in the entropy change between 593 and 603 is not much larger 1.04, 0.54, and 0.54 J K^{-1} mol^{-1} for 44, 50, and 57 at-% Sb, respectively). Such a very small increase in the entropy change corresponds to usual increase in the enthalpy due to the rise in the temperature but not due to phase transformation.

(v) Enthalpy of Formation. The data in Table 7 represent values for the integral and partial molar enthalpy of formation at 573 K as obtained from the present study for the compositions 44, 50, and 57% Sb. A number in parenthesis is the estimated standard deviation (esd). The present data of h^F could confirm those obtained earlier[2)] by using the Wittig's calorimeter.[7)] This means that the present calorimeter could be useful for measurements of heat contents with an accuracy of 0.8% and reproducibility of 0.3%.

Table 7. Integral and Partial Molar Enthalpies of Formation in the System Tin–Antimony at 573 K in J mol^{-1}. Estimated Standard Deviations in Parenthesis

x_2	$-h^F$	$-h_1^F$	$+h_2^F$
0.44	3986(13)	9242	2606
0.50	3216(12)	10158	3752
0.57	2152(11)	11506	4924

From curve-fitting calculations, the following polynomial function for h^F is derived:

$$h^F = -5.655 - 4.101x_2 + 18.01x_2^2 \tag{7}$$

This equation would produce a curve for h^F similar to that one illustrated in Figs. 2 and 3 in the previous study.[2)]

For the partial molar enthalpies of formation of tin and antimony, the following equations are derived:

$$h_1^F = -5.655 - 18.01x_2^2 \tag{8}$$

$$h_2^F = 8.254 - 18.01(x_2 - 1)^2 \tag{9}$$

These equations would also produce nearly the same curves as shown earlier.[2)] The behavior of the enthalpy of formation and its partial quantities in relation to the composition has been discussed previously.[2)] Also the behavior of the enthalpy of mixing and its partial quantities in relation to that of the enthalpy of formation is found as predicted earlier.[2)] The discussion on the data of h^F will be here restricted to the dependence of h^F on the temperature and the transformation from β' to β phase.

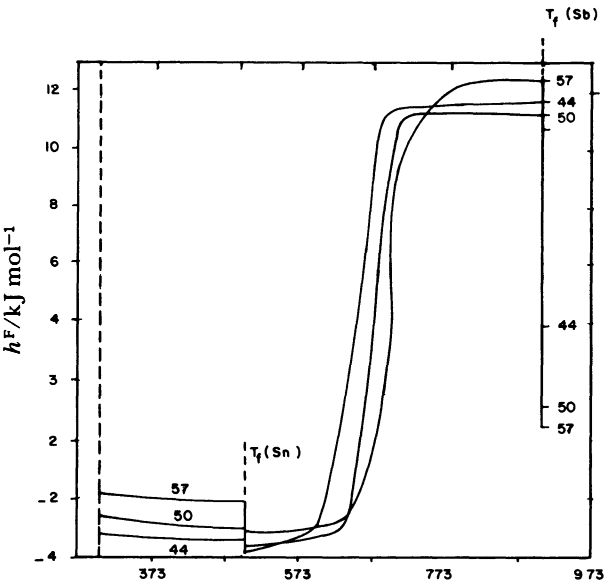


Fig. 3. Dependence of the enthalpy of formation, h^F, at the compositions 44, 50, and 57 at-% Sb on the temperature T.

With reference to the previous data,[2] the enthalpy of formation depends insignificantly on the temperature. This is only valid for the range 298.15 to 504 K. As shown in Fig. 3, h^F changes abruptly at the same temperatures around 505 and 904 K at the three compositions 44, 50, and 57 at-% Sb. This is due to the melting of Sn and Sb. Figure 3 also illustrates that h^F displays a pronounced temperature dependence above 623, 648, and 668 K at 44, 50, and 57 at-% Sb, respectively. This is due to the fact that the alloy can not persist until 623 K but partially melts in accordance with the phase diagram. The continuous formation of the liquid phase should be accompanied with continuous increasing enthalpy of formation. After completion of the liquid formation and disappearing of the β' phase, h^F increases insignificantly and drops finally due to the melting of antimony at 904.02 K (see Fig. 3).

Assuming that a β phase could exist at 598 K in equilibrium with the original one (β' phase), the entropy change for the sample with x_2=0.44 at 598 K would be

$$\Delta S = S(\beta) + S(\text{liquid}) - S(\beta') = n_s \cdot S^F_{x_s} + n_l[(1 - x_l)S^{\text{fus}}_{\text{Sn}} + x_l \cdot S^{\text{fus}}_{\text{Sb}} + S^M_{x_l}] - S^F_{x_2} \qquad (10)$$

where $S^F_{x_s}$ and $S^F_{x_2}$ are the entropies of formation at the mole fractions of the solid x_s and antimony x_2, respectively. $S^{\text{fus}}_{\text{Sn}}$ and $S^{\text{fus}}_{\text{Sb}}$ refer to the entropies of Sn and Sb, respectively. $S^M_{x_l}$ is the entropy of mixing at the mole fraction of the liquid x_l.

With reference to the phase diagram of the system Sn-Sb[4] and applying the level rule, the number of moles of the liquid will be $n_l = \frac{x_2 - x_s}{x_l - x_s} = 0.132$ mol, and that of the solid is $n_s = 1 - n_l = 0.868$ mol (x_l=0.216; x_s=0.474; x_2=0.44).

Substitution of these values in Eq. 10 together with the entropy terms, yields

$$\Delta S = [(-0.868 \times 5.644) + 0.132\{(0.784 \times 13.916^{6)}) + (0.216 \times 21.589^{6)}) - 2.408^{7)}\} + 6.366]\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta S = [3.205]\ \text{J K}^{-1}\ \text{mol}^{-1}.$$

The value of ΔS (3.205 J K^{-1} mol^{-1}) seems to be too large compared with that obtained for the increase in the change of the entropy between 593 and 603 K as 1.04 J K^{-1} mol^{-1} (see, Table 6 and p. 283). This means that our assumption of the existence of further β phase in equilibrium with the β' phase was incorrect and hence the first one seems not to be present. These views together with the above cited ones (C_p and [$h_3(T) - h_3$(298.15 K)] behavior around 598 K (the transformation temperature), estimated entropy terms and the results of the high temperature diffraction study) exclude a transformation from β to β' phase. It is also noteworthy that some strong views support the existence of only one phase.[9]

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