# Thermodynamic Properties of Alloys and Phase Equilibria in the In–Sb System

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**Abstract**—New thermodynamic data for the In–Sb system are obtained and compared with calculation results available in the literature. An isothermal vacuum cell and a procedure for electrolyte preparation are described which ensure high measurement accuracy.

## INTRODUCTION

III–V semiconductors and their solid solutions find wide application in optoelectronics and high-speed electronic devices.

The In–Sb system is often used to check the accuracy of measurements with liquid-electrolyte electrochemical cells. In addition, In–Sb alloys are used as internal standards in studies of multicomponent Inbased systems.

The phase relations in the In–Sb system are very simple (Fig. 1) [1]. It contains only one intermediate phase with a nearly perfect stoichiometry (zinc-blende structure, a = 0.6479 nm, congruent melting at 800 K). InSb and Sb form a eutectic at  $x_{Sb} = 0.688$  with a melting point  $T_{e1} = 767.3$  K. The In-rich eutectic is nearly degenerate, with a melting point ( $T_{e2} = 427.5$  K) close to that of pure indium (429.75 K).

This paper reports on the thermodynamic properties of In–Sb alloys and describes in detail the emf measurement procedure developed earlier, which was repeatedly tested in studies of various metal and semiconductor systems.

#### **EXPERIMENTAL**

**Electrolyte preparation.** This step is of key importance in emf studies. The optimal process for salt dehydration, developed earlier in our laboratory, is as follows: Salts are first dried in vacuum (0.1–1 Pa) for 30– 40 h without heating. Next, the temperature is gradually (3–5 days) raised to 150–200°C, and the hot salts are transferred to gas-tight containers. The salts are weighed and mixed in a dry box and then again closed in the containers. If there is no dry box, the most hygroscopic salt is weighed in a gas-tight container of known weight, and less hygroscopic salts are weighed by a standard procedure. The salt mixture is dehydrated in vacuum for about 1 day at a temperature slightly above 100°C and then transferred to a silica beaker preheated to 500°C in an electrical furnace. To remove oxychlorides, the molten salts are treated with HCl and  $Cl_2$ gases. After drying under optimal conditions, the melt contains insignificant amounts, if any, of oxychlorides (dark gray flakes). In addition, the melt may contain carbon particles resulting from the carbonization of organics. The melt temperature is then increased to 600–650°C, which ensures rapid burnout of the carbon. The presence of carbon particles in the salt melt may lead to the shorting of the cell electrodes.

In removing oxychlorides, one can use commercially available or laboratory-produced HCl and  $Cl_2$ gases. Hydrogen chloride can easily be synthesized by reacting KCl or NaCl with concentrated  $H_2SO_4$ . The appropriate apparatus and the preparation of gaseous compounds of HCl, HBr, and HI are described in [2]. The apparatus should contain no rubber or plastic tubing. All its parts must be made of glass or quartz and



Fig. 1. Phase diagram of the In–Sb system [1].



Fig. 2. Schematic of the isothermal cell.

must be fitted with ground-glass joints. A proven lubricant for such joints is concentrated  $H_2SO_4$ .

Hydrogen chloride must be dried using zeolites loaded into a U-tube. (Phosphoric anhydride is unsuitable because phosphoric acid vapor is transported by the gas stream to the electrolyte.) The zeolite is regenerated by calcination at 300°C immediately before assembling the apparatus. The gas is bubbled through the melt until there are no suspended particles (~1 h). The electrolyte must be transparent, with a light yellow color owing to the dissolved hydrogen chloride. After the hydrogen chloride flow is turned off, the coloration disappears rapidly because of the HCl volatilization. The melt thus prepared is poured into Pyrex tubes with a neck, which are then sealed. The electrolyte can be stored indefinitely in sealed tubes and used as required. Mechanical purification of molten salts is impermissible. The addition of ammonium chloride to the melt, proposed by Wagner and Werner [3], is inefficient.

Amount of potential-forming ions in the electrolyte. In spite of the large number of studies dealing with emf measurements in molten salts, there is no agreement as to the content of the salt of the potential-forming ion, which was varied from 0.05 to 5-7 wt % [4, 5]. According to Wagner and Werner [3], the content of the salt of the potential-forming metal must be 1-3 wt %. Our experiments indicate that the optimal content of such a salt is 0.05 to 0.1 wt %. In the case of extremely hygroscopic salts (e.g., ZnCl<sub>2</sub> and AlCl<sub>3</sub>) or rare-metal salts (InCl and LuCl<sub>3</sub>), it is possible to dispense with salt additions, since the salts form when hydrogen chloride or chlorine (dissolved in small amounts in the electrolyte) is brought into contact with the metal:

$$In(l) + HCl(g) \longrightarrow InCl + H_2(g), \qquad (1)$$

$$Lu(s) + HCl(g) \longrightarrow LuCl_3 + H_2(g).$$
 (2)

We performed experiments with In-, Sn-, Zn-, Pb-, and Lu-based alloys with (0.05 wt %) and without additions of a salt of the potential-forming ion [6–10]. The additions were found to have an insignificant effect on the emf, causing a slight decrease in the emf equilibration time ( $\leq 2$  days).

**Isothermal electrochemical cell.** Figure 2 shows a schematic of the isothermal Pyrex cell used in this study. The lower part of the cell (below the dashed line) is 54–58 mm in diameter and ~90 mm in height. The tungsten current leads and the electrodes attached to them are soldered in inlet tubes 8 mm in diameter. The bottom of the cell has cruciblelike holes, which enables studies of both solid and liquid alloys, with no risk of accidental mixing.

The upper part of the cell, ~400 mm in length and 25 mm in diameter, fitted with a ground-glass joint, serves as a container for the electrolyte. The time needed to withdraw the ingot from the tube, introduce it into the container, and connect the container to the vacuum system does not exceed 10 s.

After pumping the cell  $(10^{-3} \text{ to } 10^{-4} \text{ Pa})$  for a day, followed by flushing with purified argon, the ingot is melted under dynamic vacuum using a portable gas torch. The melt drains down into the lower part of the cell, which is introduced into a microfurnace heated to  $50-100^{\circ}$ C above the melting point of the eutectic mixture. Next, the cell is sealed off at the neck under vacuum and transferred to a preheated working furnace. A calibrated Pt/Pt–10% Rh thermocouple is introduced into the center of the cell and is level with the electrodes and electrolyte.

Such cells can operate indefinitely between the solidification temperature of the eutectic melt and the onset of softening (870 K). In the latter stages of experiments, the temperature can be raised to 900 K.

Synthesis of alloys. The alloys were prepared from weighed mixtures (~1.6 g) of high-purity (5N) indium and antimony, which were sealed in Pyrex tubes under a vacuum of  $10^{-4}$  Pa or better. The mixtures were reacted at 800 K for 48 h in resistance furnaces. The resultant ingots were up to 5 mm in diameter and 10 mm in length. In each experiment, a whole ingot was used. The difference in weight between the starting mixture and ingot was within 0.05%. The compositions of the alloys studied are listed in Table 1.

Equipment and emf measurements. The temperature in the resistance furnaces was controlled to an accuracy of  $\pm 0.2^{\circ}$ C. In emf measurements, we used a



**Fig. 3.** Temperature-dependent emf data obtained in this work for In–Sb alloys with  $x_{Sb} = (1) 0.5520$ , (2) 0.5717, (3) 0.6002, and (4) 0.5002 in comparison with earlier results: (5) [13], (6) [12], (7) [1].

Keithley Model 193 digital voltmeter with an internal resistance of  $10^{14} \Omega$  and accuracy of  $\pm 2 \mu V$ . The electrolyte used in concentration cells

(-) W, 
$$In(l) | In^+$$
 in electrolyte  $| In_x Sb_{1-x}(s), W(+) \rangle$ 

was a eutectic mixture of LiCl and RbCl (46 wt % LiCl,  $T_{\rm e} = 625$  K). The In<sup>+</sup> ions in the cell were formed by reaction (1).

The system was considered to be in equilibrium if the measured emf *E* varied by no more than  $\pm 5 \,\mu$ V over three or four measurement cycles performed at 30-min intervals. The *E*(*T*) data obtained during the first week of measurements were thought of as corresponding to a quasi-equilibrium state and were left out of consideration. The reproducibility in each series of measurements (two or three heating cycles) was  $\pm 0.7 \,\text{mV}$  or better. Measurements with each cell took 2–3 months.

#### **RESULTS AND DISCUSSION**

The emf is related to thermodynamic quantities by

$$\Delta \mu_{\rm In} = -FE = RT \ln a_{\rm In},\tag{3}$$

$$\Delta \mu_{\rm In} = \Delta \overline{H} \,({\rm In}) - T \Delta \overline{S} \,({\rm In}), \tag{4}$$

$$\Delta \overline{H} (\text{In}) = \Delta \mu_{\text{In}} - T \left( \partial \Delta \mu_{\text{In}} / \partial T \right)_n, \tag{5}$$

where F = 96485.31 C/mol, R = 8314.17 J/(mol K),  $\Delta \mu_{In}$  is the change in the chemical potential of indium,

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 $\Delta \overline{H}$  (In) is the partial enthalpy of indium, and  $\Delta \overline{S}$  (In) is the partial entropy of indium.

The E(T) data for single-phase liquids and InSb(s) + Sb(s) mixtures (Fig. 3) were fitted to equations of the form [11]

$$E = a + bT,$$

where  $a = -\Delta \overline{H} (\text{In})/F$  and  $b = \Delta \overline{S} (\text{In})/F$ . The least squares fitting results are presented in Table 2.

The E(T) values for 87 points in the InSb(s) +  $L_1$  field at temperatures from 767 to 800 K are listed in Table 3.

To compare the present thermodynamic data for In– Sb melts with the reference partial functions of mixing

Table 1. Compositions of In-Sb alloys for emf studies

x <sub>In</sub>	x <sub>Sb</sub>
0.4998	0.5002
0.4480	0.5520
0.4283	0.5717
0.3998	0.6002

No.	Phase region	x <sub>Sb</sub>	<i>a</i> , mV	$b \times 10^2$ , mV/K	l	$\overline{T}$ , K	$\overline{E}, \mathrm{mV}$	$S_0^2 \times 10^2,$ mV <sup>2</sup>	$\sum_{\substack{K^2}} (T_i - \overline{T})^2,$	$T_{\min} - T_{\max},$ K
1	InSb + Sb	0.5520	360.82	-26.63	186	710.29	171.68	52.1	168973	657–766
		0.5717								
		0.6002								
2	$L_1$	0.5002	61.90	4.68	104	815.17	100.06	88.8	34601	773–862
3	$L_1$	0.5717	64.43	7.04	69	807.48	121.30	7.2	17890	762–835
4	$L_1$	0.6002	67.46	7.83	14	795.31	129.75	2.0	3079	768–819

**Table 2.** E(T) fitting results for In–Sb alloys

Note: *l* is the number of data points, and  $S_0^2$  is the mean-square deviation.

**Table 3.** E(T) data for the InSb(s) +  $L_1$  region

Т, К	E, mV	Т, К	E, mV	Т, К	<i>E</i> , mV	Т, К	E, mV
$x_{\rm Sb} = 0.5002$		$x_{\rm Sb} = 0.5520$		$x_{\rm Sb} = 0.5717$		$x_{\rm Sb} = 0.6002$	
774	152.5	778.9	141.2	771.4	153.97	770.1	154.26
770	156.0	777.0	144.25	774	150.97	772.0	152.10
775	150.4	775.0	146.6	772	153.35	774.2	149.55
778	146.0	773.1	149.3	774.7	149.86	776.1	147.03
785	136.9	770.7	152.46	776.7	147.5	778.0	144.72
795	117.3	771.4	151.7	779.5	144.8	779.7	142.18
775	150.2	769.3	153.85	781.4	142.16	782.2	139.35
778	146.2	767.5	154.9	783.3	139.07	784.0	135.97
792	125.4	769.8	153.38	785.3	136.2	780.8	140.44
797	111.6	771.6	150.92	783.1	139.2	779.1	143.46
795	118.2	774.4	148.05	786.8	133.28	777.6	145.75
790	128.0	776.2	145.85	788.8	129.49	775.2	148.37
780	144.6	778.3	143.2	769.6	155.73	771.5	151.03
782	140.6	780.4	140.5	771.5	153.5	771.0	153.33
787	134.5	781.8	138.1	773.7	151.24	768.4	155.69
792	125.1	784.1	135.38	775.6	148.75	782.0	139.30
794	119.2	788.2	128.7	777.7	146.35	784.1	136.04
796	115.5	789.8	124.75	779.9	143.58		
798	108.0			782.0	140.92		
769	155.8			784.0	137.85		
784	137.6			786.0	134.86		
789	128.0			787.8	131.69		
793	119.5						
795	114.0						
793	122.0						
795	116.8						
799	101.3						

No.	Phase region	x <sub>Sb</sub>	$-\Delta G(\text{In}),$ kJ/mol	<i>Т</i> , К	–Δ <i>H</i> (In), kJ/mol	$\Delta S(\text{In}), \\ J/(\text{mol } K)$	Method	Source
1	InSb(s) + Sb(s)	0.5520	$16.83\pm0.1$	700	$34.81 \pm 0.24$	$-25.69\pm0.4$	EMF	This work
		0.5717						
		0.6002						
2	InSb(s) + Sb(s)	0.5990	$17.06\pm0.1$	700	$33.34 \pm 1.7$	$-23.25 \pm 2.1$	EMF	[13]
		0.6720						
3	InSb(s)			700	$35.4 \pm 1.6$		Calorimetry	[12]
4	InSb(s) + Sb(s)		$17.0 \pm 0.3$	700	$35.1 \pm 0.3$	$-25.8\pm0.3$	Calculation	[14]
5	$L_1$	0.5002	$9.58\pm0.02$	800	$5.97 \pm 0.4$	$4.52\pm1.0$	EMF	This work
6	$L_1$	0.5717	$11.65\pm0.01$	800	$6.22 \pm 0.3$	$6.79\pm0.4$	EMF	This work
7	$L_1$	0.6002	$12.55\pm0.01$	800	$6.51\pm0.3$	$7.55\pm0.4$	EMF	This work

Table 4. Partial thermodynamic functions of formation of In-Sb alloys

 $\Delta \overline{H}$  (In) and  $\Delta \overline{S}$  (In) [14], the latter were represented in the form

$$\Delta \mu_{\rm In} = x_{\rm Sb} (2317.8 - 30577 x_{\rm Sb} + 19301 x_{\rm Sb}^2) + 9.4T \ln(1 - x_{\rm Sb}),$$
(6)

with an accuracy of  $\pm 100$  J/mol in the range 0.1 <  $x_{Sb}$  < 0.5 and  $\pm 250$  J/mol in the range 0.6 <  $x_{Sb}$  < 0.9.

The thermodynamic functions of formation of solid In–Sb samples [12, 14] (Table 4) are given for the In(l) and Sb(s) states at 700 K. The data necessary for calculations were taken from [12, 15].

The enthalpy of fusion of InSb was evaluated using the present data (Table 4, nos. 1, 5) and the enthalpy of fusion of antimony reported in [15]. The results are presented in Table 5.

In the proper temperature and composition ranges, the present emf results for In–Sb alloys are in excellent agreement with the optimized data reported by Ansara *et al.* [1] for melts. In the two-phase regions InSb + Sb and InSb +  $L_1$ , the data differ somewhat. At the same time, the results of earlier calculations by Degtyarev and Voronin [14] agree well with the present thermodynamic functions of formation of solid InSb (Table 4). It

 Table 5. Heat of InSb fusion

Source	[15]	[12]	This work
$\frac{\Delta_{\rm m} H({\rm InSb})}{\rm kJ/mol},$	$_{\rm m}H({\rm InSb}),$ 48.5 ± 2 //mol		$48.66 \pm 0.5$

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seems likely that the optimized data in [1] need correction.

## CONCLUSIONS

The present results demonstrate that In–Sb alloys are ideally suited for checking the accuracy of measurements with liquid-electrolyte electrochemical cells and for use as internal standards in studies of multicomponent In-based systems.

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