

# The In-Sb (Indium-Antimony) System

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## Equilibrium Diagram

### Ambient-Pressure Equilibria

The In-Sb system is characterized by a congruently melting intermediate phase,  $\alpha$ InSb, that forms at 50 at.% Sb and two eutectic reactions, one each in the In-InSb and InSb-Sb regions of the phase diagram. Deviation from stoichiometry in the  $\alpha$ InSb phase is negligible. The assessed In-Sb phase diagram, (Fig. 1 and 2) is based on the present evaluators' modeling and calculations.

The melting points of In and Sb are 156.643 and 630.755 °C, respectively [Melt]. The liquidus was determined by [49Pog], [52Liu], [63Hal], and [83Gor]. The calculated liquidus shown in Fig. 1 and 2 agrees well with the experimental data, except that at low concentrations (Fig. 2), the data of [63Hal] do not agree well with the assessed liquidus. [63Hal] determined the liquidus by dissolving small crystals of  $\alpha$ InSb in known amounts of In liquid and measuring the weight loss of the crystals to determine the solubility. In the present evaluators' opinion, the method is prone to significant errors, particularly for low solubilities. The assessed liquidus close to pure In, however, agrees well with the

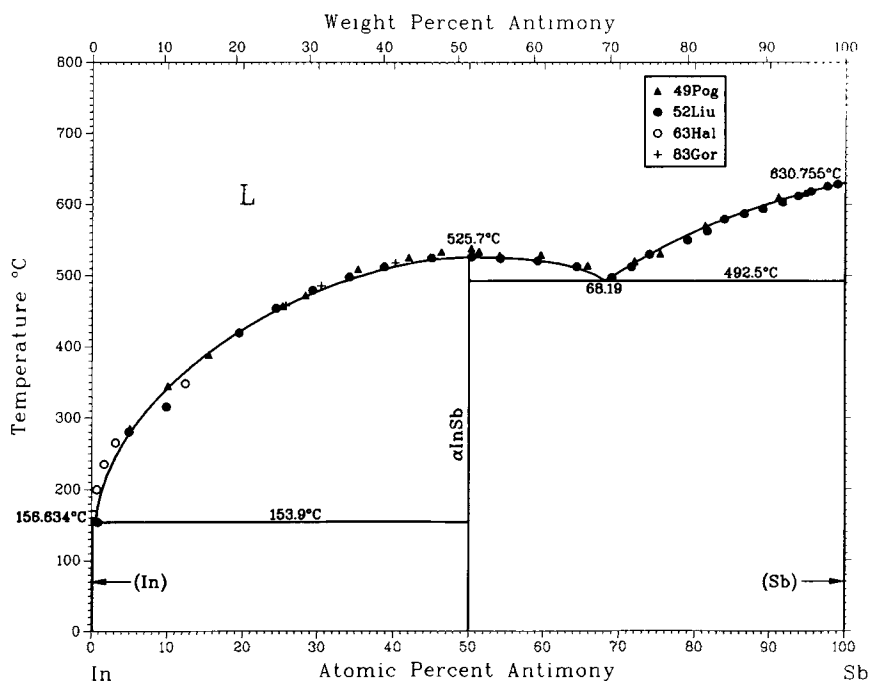
eutectic composition (0.66 at.% Sb at 154 °C) determined by [52Liu] by the same technique. Table 1 gives the assessed liquidus values.

The mutual solid solubilities of In and Sb are negligible [52Liu] and have not been experimentally determined.

The  $\alpha$ InSb is essentially a stoichiometric compound. Using precision lattice parameter measurements, [63Ozo] and [65Str] showed that the equilibrium homogeneity range of  $\alpha$ InSb is negligible. [81Zai] calculated the homogeneity range of  $\alpha$ InSb from theoretical considerations and showed that  $\alpha$ InSb may be slightly In-rich; however, there is no experimental confirmation of this premise. The congruent melting point of  $\alpha$ InSb, as determined by different investigators, is given in Table 2 with the assessed value.

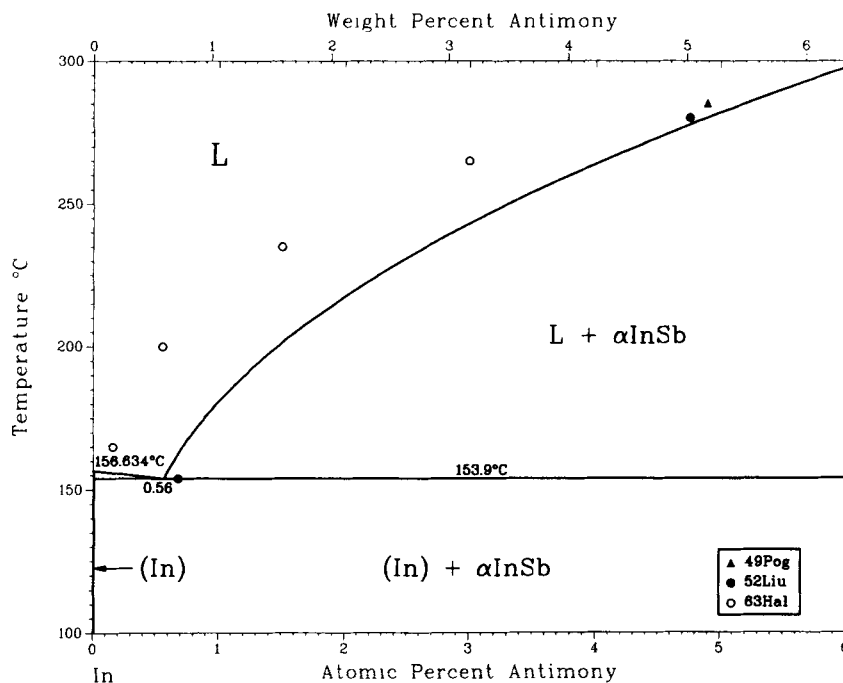
Table 3 summarizes the experimental data cited in the literature for the invariant equilibria in the In-Sb system, as well as the assessed values. The In-Sb phase diagram has been calculated using the thermodynamic data described below. Agreement between the calculated and experimental phase diagram is good. The assessed phase diagram (Fig. 1 and 2) is based on calculations completed by the present evaluators. [71Bre1],

Fig. 1 Assessed In-Sb Phase Diagram



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Fig. 2 In-Rich Region of the In-Sb Phase Diagram



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Table 1 Assessed In-Sb Liquidus

Composition, at.% Sb	Temperature, °C	Composition, at.% Sb	Temperature, °C
0	156.643	60	514.8
10	347.7	70	505.0
20	426.5	80	561.4
30	480.8	90	599.4
40	514.3	100	630.755
50	525.7		

[71Bre2], [77Bre], [80Sza], [81Kau], [82Lia], and [83Bre] also calculated the In-Sb phase diagram.

#### High-Pressure Equilibria

[60Geb], [63Ban], [63Jay], [64Dar], [64Kas], [67Ban], [69Ban], [71Ome], [78Yu], and [82Tur] have studied the  $P$ - $T$  phase equilibria for the pseudo-single-component InSb phase. The results of these investigations are generally consistent. The  $P$ - $T$  phase diagram for InSb, based on these investigations, is given in Fig. 3. In addition to the  $\alpha$ InSb phase, which is formed at atmospheric pressures, three high-pressure modifications occur (Fig. 3)— $\beta$ InSb,  $\gamma$ InSb, and  $\delta$ InSb. The melting point of  $\alpha$ InSb (525.7 °C at 1 atm) decreases with increasing pressure at the initial rate of  $\sim 10$  °C/kbar, and the melting point of  $\gamma$ InSb increases at the rate of  $\sim 2.3$  °C/kbar near the  $L$ - $\alpha$ InSb- $\gamma$ InSb triple point [63Jay]. The coordinates of the different triple points in the  $P$ - $T$  phase diagram (Fig. 3) of InSb are given in Table 4.

Table 2 Melting Temperature of  $\alpha$ InSb

Reference	Melting Point, °C
[49Pog]	536
[63Lun]	530
[52Liu]	525 $\pm$ 5
[77Gar]	525 $\pm$ 5
[55Bed]	525.2 $\pm$ 0.3
[58Sch]	525
[65Ric]	525.0 $\pm$ 1.0
[67Cox]	525
[69Lic]	524
[Hansen]	530 $\pm$ 5
Assessed	525.7

[79Deg], [81Deg2], [82Deg], and [83Deg] studied high-pressure phase formation in In-Sb alloys of varying composition ( $\sim 20$  to 80 at.% Sb) at different temperatures. From these studies, they concluded that in the pressure-temperature-composition ( $P$ - $T$ - $C$ ) phase space, InSb cannot be considered as a pseudo-single-component system. For a 50 at.% Sb alloy, they observed two phases in equilibrium at certain pressures and temperatures in the single-phase stability regions of  $\gamma$ InSb and  $\delta$ InSb given in Fig. 3. This suggests that the 50 at.% Sb plane in the  $P$ - $T$ - $C$  phase space cuts through the two phase regions [83Deg].  $\beta$ InSb at 38 kbar and 175 °C was found to be stable from 50 at.% Sb to 55 at.% Sb [83Deg]. They also observed several additional high-pressure phases in the In-Sb system at dif-

**Table 3 Invariant Equilibria in the In-Sb Phase Diagram**

Reaction	Composition of the respective phases, at.% Sb			Temperature, °C	Reaction type	Reference
L ↔ (In) + αInSb.....	0.66	~0	50	154.89	Eutectic	[52Liu]
	...	0	50	155		[49Pog]
	0.56	.0	50	153.9		Assessed
L ↔ αInSb + (Sb).....	70.4	50	100	506 ± 2	Eutectic	[49Pog]
	68.3	50	100	494 ± 3		[52Liu]
	68.19	50	100	492.5		Assessed

**Table 4 Triple Points in the In-Sb P-T Phase Diagram**

Phases in Equilibrium	Pressure, kbars	Temperature, °C	Reference
L + αInSb + γInSb .....	19.4	335	[63Jay]
αInSb + βInSb + γInSb.....	20	317	[67Ban]
βInSb + γInSb + δInSb.....	65	175	[69Ban]
αInSb + βInSb + δInSb .....	~23.5	30 to 50	[69Ban,82Tur]

**Table 5 High-Pressure Phases in the In-Sb System**

Phase(a)	Composition, at.% Sb	Pressure, kbar	Temperature, °C
ξ .....	40	70	350
γ <sub>1</sub> (βInSb).....	50-55	38	175
γ <sub>2</sub> .....	47.5	70	350
<<β Sn>>.....	55	70	350
π(b) .....	60-70	70	350
π' .....	57.5	18	300
ω .....	20	55	350

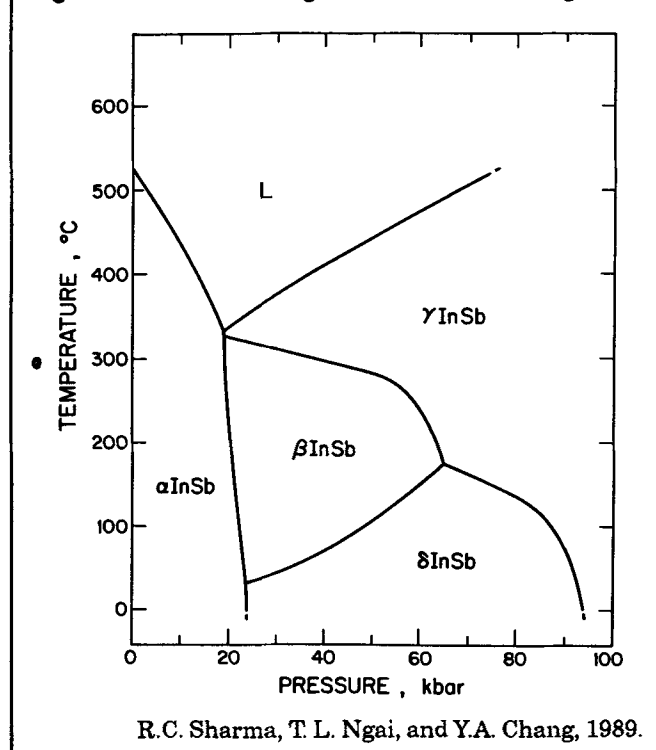
(a) Phase designations of [81Deg2] and [83Deg]. (b) Metastable phase.

ferent compositions. The different phases observed by [79Deg], [81Deg2], and [83Deg] at high pressures are listed in Table 5. The reader is referred to the original work, particularly [83Deg] for details.

### Metastable Phases

Two metastable phases have been reported in the In-Sb system. [63Jor] observed a cubic phase (π phase) in In-Sb alloys (containing ~70 at.% Sb) upon rapid quenching from the liquid phase. [76Asa] also observed a cubic phase when amorphous InSb was subjected to pressures of 4 to 28 kbar. [83Deg] found a cubic phase with lattice parameters similar to those reported by [63Jor] upon the decomposition of high-pressure <<βSn>> phase (produced at 70 kbar and 350 °C) at temperatures >15 °C and atmospheric pressures.

[57Sem], [61Pal], and [65Gie] observed a γ-type hexagonal phase in thin films of In-Sb alloys produced by either quenching from the melt [65Gie], or by sublimation of InSb [57Sem, 61Pal].

**Fig. 3 P-T Phase Diagram for the InSb Region**

### Crystal Structures and Lattice Parameters

Crystal structure and lattice parameter data of stable, metastable, and high-pressure phases observed in the In-Sb system are given in Table 6 and 7, respectively.

# In-Sb

**Table 6 In-Sb Crystal Structure Data**

Phase	Composition, at.% Sb	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
(In) .....	0	<i>tI2</i>	<i>F4/mmm</i>	A6	In	[Pearson2]
$\omega$ (a) .....	~20	<i>hP6</i>	<i>P6<sub>3</sub>/mmc</i>	<i>B8<sub>2</sub></i>	InNi <sub>2</sub>	[81Deg2]
$\zeta$ (a) .....	~40	<i>tI32</i>	<i>I4/mcm</i>	<i>D8<sub>1</sub></i>	Cr <sub>5</sub> B <sub>3</sub>	[83Deg]
$\gamma_2$ (a) .....	47.5	<i>oP4</i>	...	...	...	[83Deg]
$\alpha$ InSb .....	50	<i>cF8</i>	<i>F43m</i>	B3	ZnS	[Pearson2]
$\beta$ InSb (a) .....	50	<i>tI4</i>	<i>I4<sub>1</sub>/amd</i>	A5	$\beta$ Sn	[Pearson2]
$\gamma_1$ (a) .....	50 to 55	<i>oP2</i>	<i>Pmm2</i>	...	...	[83Deg]
$\gamma$ InSb (a) .....	50	(b)	...	...	...	[69Ban]
$\gamma$ InSb (a) .....	50	<i>oP4</i>	<i>Pmmm</i> or <i>Pmmn</i>	...	...	[78Yu]
$\delta$ InSb (a) .....	50	<i>oP2</i>	<i>Pmm2</i>	...	...	[64Kas, 69Ban, 78Yu]
<< $\beta$ Sn>> (a) .....	55	<i>tI4</i>	<i>I4<sub>1</sub>/amd</i>	A5	$\beta$ Sn	[83Deg]
$\pi'$ (a) .....	57.5	<i>hR1</i>	<i>R3m</i>	...	...	[83Deg]
$\pi$ (c) .....	60 to 70	<i>cP1</i>	<i>Pm3m</i>	<i>A<sub>h</sub></i>	$\alpha$ Po	[63Jor, 83Deg]
InSb (thin films)(c) .....	...	<i>hP4</i>	<i>P6<sub>3</sub>/mc</i>	B4	ZnS	[Pearson2]
(Sb) .....	100	<i>hR2</i>	<i>R3m</i>	A7	As	[Pearson2]

(a) High-pressure phase. (b) Hexagonal. (c) Metastable phase.

**Table 7 In-Sb Lattice Parameter Data**

Phase	Composition, at.% Sb	Temperature, °C	Pressure, kbar	Lattice parameters, nm				Reference
				<i>a</i>	<i>b</i>	<i>c</i>	$\alpha$	
(In) .....	0	25	...	0.45979	...	0.49467	...	[Pearson2]
$\omega$ (a) .....	~20	-190	...	0.5364	...	0.6408	...	[81Deg2]
$\zeta$ (a) .....	~40	-190	...	0.830	...	1.226	...	[83Deg]
$\gamma_2$ (a) .....	47.5	-190	...	0.328	0.548	0.598	...	[83Deg]
$\alpha$ InSb .....	50	25	...	0.64788	...	...	...	[Pearson2]
$\beta$ InSb (a) .....	50	...	25	0.592	...	0.306	...	[62Smi]
			25	0.579	...	0.311	...	[64Han]
			150	0.5537	...	0.2970	...	[63Jam]
		-197	...	0.572	...	0.318	...	[63Dar]
		25	...	0.579	...	0.315	...	[64Han]
		25	...	0.580	...	0.315	...	[64Kas]
$\gamma$ InSb (a) .....	50 to 55	-190	...	0.5850	0.2990	0.3117	...	[83Deg]
	50	...	125	0.6099	...	0.5708	...	[69Ban]
			115	0.5712	0.5357	0.3063	...	[78Yu]
$\delta$ InSb(a) .....	50	...	70	0.2921	0.5532	0.3093	...	[69Ban]
			44	0.2919	0.5618	0.3066	...	[78Yu]
<< $\beta$ Sn>>(a) .....	55	-190	...	0.5842	...	0.3184	...	[83Deg]
$\pi'$ (a) .....	57.5	-190	...	0.3056	...	...	89.2°	[83Deg]
$\pi$ (b) .....	60	25	...	0.3047	...	...	...	[83Deg]
	70	25	...	0.305	...	...	...	[63Jor]
InSb (thin film) (b) ..	50	25	...	0.457	...	0.747	...	[57Sem]
(Sb) .....	100	25	...	0.45067	...	...	57°6'27''	[Pearson2]

(a) High-pressure phase. (b) Metastable phase.

## Thermodynamics

### Pure Components

The enthalpies of melting given by [Hultgren, E] were used to give the Gibbs energy of melting of pure In and Sb as:

$$\Delta_{\text{fus}}G^0(\text{In}) = 3263.52 - 7.5934 T \text{ J/mol} \quad (\text{Eq 1})$$

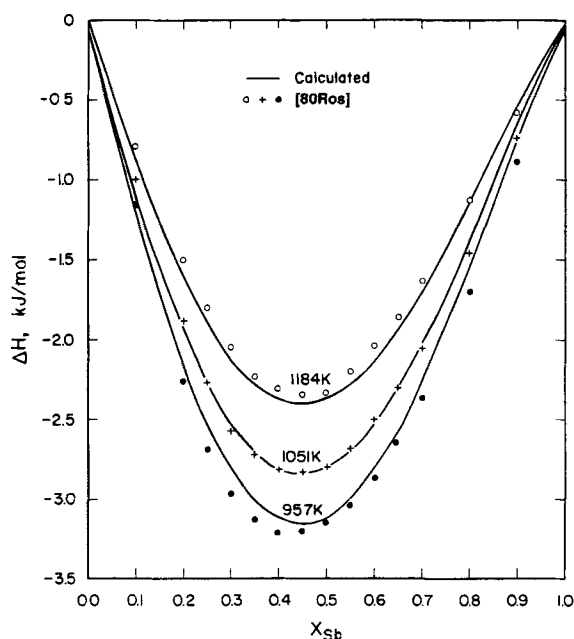
and

$$\Delta_{\text{fus}}G^0(\text{Sb}) = 19\,874.0 - 21.9868 T \text{ J/mol} \quad (\text{Eq 2})$$

### Liquid Phase

[60Ter], [65Hos], [73Cha], [83Gor], and [84And] measured the activity of In in liquid In-Sb alloys in the temperature range 643 to 1073 K by the EMF method. The enthalpy of mixing in the liquid was measured by [67Wit], [68Yaz], [74Vec], [75Ita], [76Pre], [77Ita], [78Oeh], and [80Ros] at various temperature. The following polynomial solution model has been used to describe the excess Gibbs energy of mixing in the liquid alloys:

$$\Delta G^{\text{ex}} = x_{\text{In}} x_{\text{Sb}} [Ax_{\text{In}} + Bx_{\text{Sb}} + Cx_{\text{In}}x_{\text{Sb}}] \quad (\text{Eq 3})$$

**Fig. 4** Calculated vs Experimental Enthalpy of Mixing of Liquid Alloys

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**Table 8** Thermodynamic Data for the Liquid Phase

$$A = -28\,842.3 + 128.293 T - 16.312 T \ln T \text{ J/mol}$$

$$B = -16\,184.0 + 76.165 T - 9.9435 T \ln T \text{ J/mol}$$

$$C = -9\,985.86 - 10.742 T \text{ J/mol}$$

$$\text{Note: } \Delta G_{\text{ex}}(L) = x_{\text{In}}x_{\text{Sb}} [Ax_{\text{In}} + Bx_{\text{Sb}} + Cx_{\text{In}}x_{\text{Sb}}]$$

The partial excess Gibbs energy of mixing for In and Sb are then given as:

$$\Delta \bar{G}_{\text{In}}^{\text{ex}} = x_{\text{Sb}}^2 [2Ax_{\text{In}} + B(1-2x_{\text{In}}) + Cx_{\text{In}}(2-3x_{\text{In}})] \quad (\text{Eq 4a})$$

and

$$\Delta \bar{G}_{\text{Sb}}^{\text{ex}} = x_{\text{In}}^2 [A(1-2x_{\text{Sb}}) + 2Bx_{\text{Sb}} + Cx_{\text{Sb}}(2-3x_{\text{Sb}})] \quad (\text{Eq 4b})$$

A, B, and C are expressed as a function of temperature as:

$$A = A_1 + A_2T + A_3 T \ln T \quad (\text{Eq 5a})$$

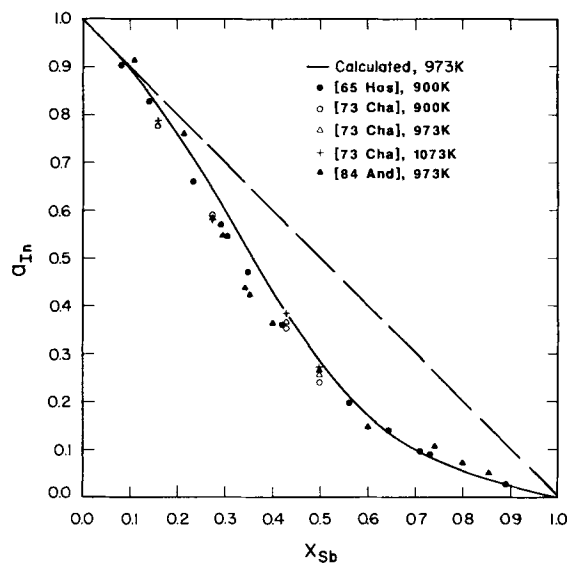
$$B = B_1 + B_2T + B_3T \ln T \quad (\text{Eq 5b})$$

and

$$C = C_1 + C_2T \quad (\text{Eq 5c})$$

The optimum values of solution parameters are obtained by using the available thermodynamic and phase equilibria data (Table 8).

Figures 4 and 5 compare the calculated and experimental data for the enthalpy of mixing and the activity of In

**Fig. 5** Calculated vs Experimental Activity of In in Liquid Alloys

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in liquid alloys, respectively. The agreement is, in general, good. In Fig. 4, only the data of [80Ros] are plotted for the sake of clarity; other data also agree well with the calculated enthalpies of mixing.

[77Bre], [77Osa], [80Sza], [81Lel], [82Lia], [82Som], [82Was] and [83Bre] described the thermodynamic properties of the In-Sb liquid phase by an associated solution model. The present evaluators have obtained as good or better fit with the experimental data by using a simpler polynomial solution model described above. It is noteworthy to add that [81Deg1] also evaluated the thermodynamic properties of the liquid phase and  $\alpha$ InSb.

#### $\alpha$ InSb Phase

[55Kle], [58Sch], [63Lun], [67Jen1], and [69Lic] measured the enthalpy of formation of  $\alpha$ InSb. [59Nik], [60Ter], [67Sir], and [70Abb] determined the Gibbs energy of formation of  $\alpha$ InSb, and [62Nac], [67Cox], and [69Lic] determined the heat content of  $\alpha$ InSb as a function of temperature. All of these data have been evaluated by [Hultgren, B]. The values selected by [Hultgren, B] for the Gibbs energy of formation of  $\alpha$ InSb from In(c) and Sb(c) are used to yield:

$$\Delta_f G^0(\alpha\text{InSb}) = -30\,252.25 - 0.2460 T + 2.4284 T \ln T \text{ J/mol of InSb} \quad (\text{Eq 6})$$

The enthalpy of melting of  $\alpha$ InSb has been determined by [58Sch], [60Ter], [62Nac], [63Lun], [65Ric], [67Cox], [69Lic], [70Bla], [76Kuz], and [77Gar]. All these data have been evaluated by [Hultgren, B] and their assessed value is used here to give the Gibbs energy of fusion for  $\alpha$ InSb as:

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$$\Delta_{\text{fus}}G^0(\alpha\text{InSb}) = 48\,097.0 - 60.215 T \quad \text{J/mol of } \alpha\text{InSb} \quad (\text{Eq 7})$$

### High-Pressure Phase

[67Jen2] and [78Jen] measured the enthalpies of formation of  $\alpha\text{InSb}$  and the high pressure modifications of  $\alpha\text{InSb}$  at 78 K and 1 atm. The high-pressure phases are metastable under these conditions. The results of these investigations are:

$$\Delta_f H^0_{78}(\alpha\text{InSb}) = -29\,790 \pm 420 \text{ J/mol}$$

$$\Delta_f H^0_{78}(\beta\text{InSb}) = -8\,700 \pm 500 \text{ J/mol}$$

$$\Delta_f H^0_{78}(\gamma\text{InSb}) = -6\,780 \pm 500 \text{ J/mol} \quad (\text{Eq 8})$$

and

$$\Delta_f H^0_{78}(\delta\text{InSb}) = -4\,602 \pm 76 \text{ J/mol} \quad (\text{Eq 9})$$

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- \*Indicates key paper.  
#Indicates presence of a phase diagram.

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## The H-Zn (Hydrogen-Zinc) System

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### Equilibrium Diagram

No phase diagram for the Zn-H system was found in a search of literature available through 1988. Normally, the presentation of a  $T$ - $X$  diagram together with a  $P$ - $X$  diagram would be required to give representative sections of a  $P$ - $X$ - $T$  surface for a complete graphical description of the equilibrium phase relationships for a metal-hydrogen system. However, in the Zn-H system, there are at present not enough  $P$ - $X$  measurements available, so that only a  $T$ - $X$  diagram can be presented.

The assessed Zn-H  $T$ - $X$  diagram at atmospheric pressure is shown in Fig. 1. The left side of the boundary shown for solid Zn represents absorption of H at very low concentrations, constituting the present limits on the maximum observed solubility, but not necessarily demarcating the range of existence of equilibrium phases. Because the amount of H dissolved in Zn is extremely small (at the pressures investigated so far), the net effect of H on lowering or raising the melting temperature of Zn (419.58 °C [83Cha]) should be scarcely measurable under these conditions.

### Solubility

The solubility of H in Zn is very small at  $P < 1$  bar (see Fig. 1). Thus in an early report, [10Sie] concluded that Zn does not dissolve H up to temperatures of 600 °C, but [23Dem] (and later [29Hen]) found that under atmospheric pressure, Zn is permeable to H at temperatures between 305 and 419.58 °C. Others [09Del, 12Gui, 24Sch, 32Ron, 35Sch] reported on the amount of H extracted from Zn metal produced by using electrolytic refining.

The results of the first quantitative study of the H solubility in Zn are not considered in the present assessment.\*

[56Hof] and [57Hof] found that molten Zn (99.995 wt.%) at a temperature of 516 °C dissolves only around  $1 \times 10^{-5}$  at.% H. The same experimental set-up was used by [56Hof] and [57Hof] to measure the solubility

\*Values determined by [26Iwa] for the H solubility in Zn, Fe, Al and other metals are consistently one or two orders of magnitude higher than values found in the available literature.