The Na-Sn (Sodium-Tin) System

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Equilibrium Diagram

The assessed Na-Sn phase diagram is given in Fig. 1, and the special points of this diagram are listed in Table 1.

Phase diagram data were obtained by thermal analysis over the entire composition range in two reports [05Mat, 28Hum]. The later study [28Hum] is more complete: more than 60 alloy compositions were used in thermal analysis, and an additional 30 compositions between 22 and 95.5 at.% Sn were used for annealing, quenching, and microscopic examination. The assessed phase diagram (Fig. 1) is based to a large extent on this work [28Hum], modified as required by more recent findings.

The solubility of Sn in liquid Na was determined from emf measurements (340 to 415 °C) [72Hub], by radiochemical analysis (120 to 257 °C) [67Lam], and by combined thermal analysis/resistance measurements (181 to 361 °C) [74Hub]. The results of these investigations are given in Table 2. The calculated solubilities of [67Lam] and [74Hub] are in good agreement in their common temperature range.

The Na-side eutectic was reported to be 97 °C [28Hum] or 97.83 °C [74Hub], the eutectic composition being practically indistinguishable from pure Na. On the assumption that there is zero solid solubility of Sn in Na, the eutectic composition may be calculated from the results of [74Hub] to be about 0.01 at.% Sn. The high-temperature eutectic was reported as 440 °C, 37.9 at.% Sn [05Mat], or 441 °C, 38 at.% Sn [28Hum]. The Sn-side eutectic was found to be 220 °C, 95.4 at.% Sn [05Mat], and 220 °C, 95.8 at.% Sn [28Hum]. The extent of solid solubility of Na in Sn could not be detected by [28Hum], who examined microscopically an annealed alloy of 95.5 at.% Sn and found only Sn and the most Sn-rich compound. Metallographic analysis [49Pok] indicated solid solubility of up to 2.5 at.% Na, but later work by the same author [61Pok] suggests that the solubility is less than 0.01 at.%. The theoretical limiting liquidus slope, calculated on the assumption of zero solid solubility, coincides within experimental uncertainty with experiment [28Hum], with a calculated eutectic composition (at 220 °C) of 96 at.% Sn. Liquidus data for alloys of compositions greater than 95 at.% Sn were obtained by freezing-point measurements [1889Hey, 1889Tam, 1890Hey]. Remaining features of the phase diagram may conveniently be discussed with reference to intermetallic compounds.

Until recently, the most Na-rich compound was believed to be "Na_4Sn," rather than $Na_{15}Sn_4$ [36Zin, 75Mul, 78Mul]. As

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Table 1 Special Points of the Assessed Na-Sn Phase Diagram

Reaction	Compositions of the respective phases, at.% Sn			Temperature, °C	Reaction type
$L \leftrightarrow (\beta Na)$		0		97.8	Melting Point
$L \leftrightarrow (\beta Na) + Na_{15}Sn_4$	≈0.01	0	21.1	97.8	Eutectic
$Na_{15}Sn_4 \leftrightarrow L + Na_9Sn_4$	21.1		30.8	408	Peritectic
$Na_{15}Sn_4 + Na_9Sn_4 \leftrightarrow Na_3Sn$	21.1	30.8	25	377	Peritectoid
$L \leftrightarrow Na_9Sn_4$		30.8		478	Congruent Point
$L \leftrightarrow Na_4Sn_3 + Na_9Sn_4$	38.0	42.9	30.8	441	Eutectic
$Na_9Sn_4 + \alpha NaSn \leftrightarrow Na_4Sn_3$	30.8	50	42.9	357	Peritectoid
$Na_4Sn_3 \leftrightarrow L + \alpha NaSn$	42.9		50	479	Petitectic
$\alpha NaSn \leftrightarrow \beta NaSn$		50		483	Allotropic Transformation
$L \leftrightarrow \beta NaSn$		50		578	Congruent Point
$NaSn_2 \leftrightarrow L + \alpha NaSn$	66.7		50	307	Peritectic
$NaSn_3 \leftrightarrow L + NaSn_2$	75.0		66.7	289	Peritectic
$NaSn_4 \leftrightarrow L + NaSn_3$	80.0		75.0	229	Peritectic
$NaSn_6 \leftrightarrow L + NaSn_4$	85.7		80.0	226	Peritectic
$L \leftrightarrow NaSn_6 + (\beta Sn)$	96.0	85.7	100	220	Eutectic
$L \leftrightarrow (\beta Sn)$		100		231.9681	Melting Point

"Na_4Sn," it was detected by emf measurements [20Kre], prepared by direct combination of the elements [11Vou, 28Hum, 67Lam] and by reaction in liquid ammonia [00Leb, 25Kra, 31Zin]. It was characterized as $Na_{15}Sn_4$ by its single-crystal [36Zin, 75Mul, 78Mul] or powder [80Guk] XRD pattern. It was reported to melt incongruently at 411 °C [67Lam], 405 °C [11Vou, 05Mat], or 408 °C [28Hum], the peritectic composition being 20 [28Hum] or 19.2 [05Mat] at.% Sn.

Na_3Sn decomposes peritectoidally at 377 °C [28Hum]. The stoichiometry was later corroborated by its powder XRD pattern [80Guk].

"Na_2Sn" was earlier thought to be the stoichiometry of a compound melting congruently at 470 °C [28Hum], 477 °C [05Mat, 11Vou], or 478 °C [28Hum]. It was later shown to be Na_9Sn_4 [78Mul]. As "Na_2Sn," it was detected by emf measure-

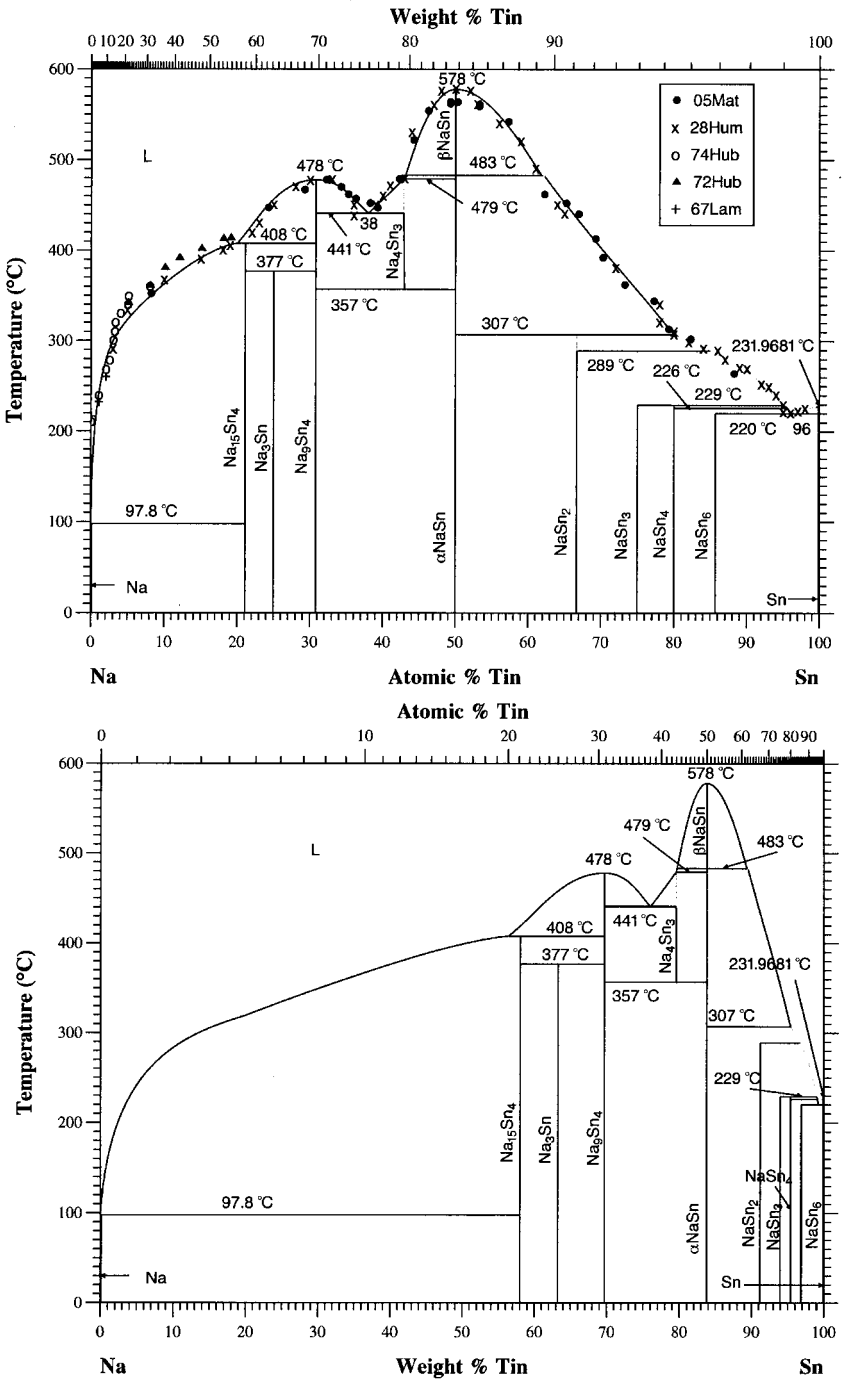

Fig. 1 Assessed Na-Sn phase diagram.

ments [20Kre] and prepared by direct reaction of the elements [1892Bai, 11Vou, 26Hum, 28Hum]. As "Na_2Sn," it was characterized by its powder x-ray pattern [80Guk] and as Na_9Sn_4 by its single-crystal x-ray pattern [78Mul].

Na_4Sn_3 melts incongruently at 478 °C [05Mat, 11Vou] or 479 °C [28Hum]. Electromotive force measurements at room temperature [20Kre] showed no indication of a compound at this stoichiometry; it was later shown [28Hum] that Na_4Sn_3 decomposes at a lower temperature (357 °C). A "transformation" temperature of 348 °C [05Mat] corresponds to this peritectoid.

NaSn was prepared by direct reaction of the elements [11Vou, 28Hum, 77Mul] and was detected by emf measurements [20Kre]. Its congruent melting point is the highest temperature on the Na-Sn liquidus: 576 °C [05Mat, 11Vou] or 578 °C [28Hum]. It undergoes a transformation at 483 °C [05Mat, 11Vou, 28Hum]. The low-temperature form was characterized by its single-crystal [77Mul] and powder [80Guk] XRD patterns.

$NaSn_2$ was prepared by direct reaction of the elements [11Vou] and in liquid ammonia [26Ber]. It was detected in emf measurements at room temperature [20Kre]. It melts incongruently at 305 °C [28Hum] at a peritectic composition of 80.6 at.% Sn [05Mat, 28Hum]. A "transformation" temperature of 224 °C [05Mat] was probably confused with the cluster of peritectics and eutectic in this system lying between 220 ° and 229 °C [28Hum].

$NaSn_3$ melts incongruently at 289 °C at a peritectic composition of 86 at.% Sn [28Hum]. A compound of approximately this stoichiometry was thought to be responsible for physical changes in the cathode material during polarization measurements [02Hab, 03Sac].

$NaSn_4$ melts incongruently at 229 °C at a peritectic composition of 95 at.% Sn [28Hum]. It was prepared by direct reaction of the elements and characterized by its powder xray pattern [69Bru] which, because of its complexity, could not be analyzed.

$NaSn_6$ melts incongruently at 226 °C and a peritectic composition of 95.3 at.% Sn [28Hum].

No range of stoichiometry could be detected by thermal and microscopic analysis for any of the intermediate compounds

Table 2 Experimentally Determined Solubility of Sn in Liquid Na

Temperature range, °C	*a*	*b*	Reference
98 to 321	10.705	–5623	[74Hub]
120 to 257	9.895	–5270	[67Lam]
340 to 415	12.48	–6579	[72Hub]

$\ln$ (at.% Sn) = $a + b/T$(K)

Table 3 Na-Sn Crystal Structure Data at 25 °C

Phase	Composition, at.% Sn	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
αNa(a)	0	*hP*2	$P6_3/mmc$	*A*3	Mg	[Massalski2]
βNa	0	*cI*2	$Im\bar{3}m$	*A*2	W	[Massalski2]
$Na_{15}Sn_4$(b)	21.1	*oP*40	*Pnma*	…	$Na_{15}Sn_4$	[75Mul]
$Na_{15}Sn_4$	21.1	*cI*76	$I\bar{4}3d$	$D8_6$	$Cu_{15}Si_4$	[78Mul]
Na_9Sn_4	30.8	*oC*52	*Cmcm*	…	Na_9Sn_4	[78Mul]
αNaSn	50.0	*tI*64	$I4_1/acd$	…	NaPb	[77Mul]
αSn(c)	100	*cF*8	$Fd\bar{3}m$	*A*4	C(d)	[Massalski2]
(βSn)	100	*tI*4	$I4_1/amd$	*A*5	βSn	[Massalski2]

(a) <36 K. **(b)** The exact stoichiometry is given as $Na_{3.7}Sn$ by [75Mul]. **(c)** <18 °C.

Table 4 Na-Sn Lattice Parameter Data at 25 °C

Phase	Composition, at.% Sn	Lattice parameters, nm *a*	*b*	*c*	Reference
αNa(a)	0	0.3767	…	0.6154	[Massalski2]
βNa	0	0.42906	…	…	[Massalski2]
$Na_{15}Sn_4$(b)	21.1	0.982	0.557	2.279	[75Mul]
$Na_{15}Sn_4$	21.1	1.314	…	…	[78Mul]
Na_9Sn_4	30.8	0.542	0.939	2.962	[78Mul]
αNaSn	50.0	1.046	…	1.739	[77Mul]
αSn(c)	100	0.64892	…	…	[Massalski2]
βSn	100	0.58316	…	0.31818	[Massalski2]

(a) <36 K. **(b)** The exact stoichiometry is given as $Na_{3.7}$ Sn by [75Mul]. **(c)** <18 °C.

[28Hum], and hence no solid solution is indicated in the assessed phase diagram.

Crystal Structures and Lattice Parameters

Crystal structure and lattice parameter data are summarized in Tables 3 and 4. The XRD pattern of single-crystal $Na_{15}Sn_4$ was determined on three occasions [36Zin, 75Mul, 78Mul]. In the two earlier determinations [36Zin, 75Mul], orthorhombic symmetry was found and the lattice parameters were quite similar: a = 0.979 nm, b = 2.278 nm, c = 0.556 nm [36Zin]; a = 0.982 nm, b = 0.557 nm, c = 2.279 nm [75Mul]. From the pycrometrically measured density, the number of atoms per unit cell was calculated to be 40 [36Zin], although the expected number was 38 (=2*X*19) [36Zin]. These authors [36Zin] believed that $Na_{15}Sn_4$ and $Na_{15}Pb_4$ had "probably closely related" structures, although $Na_{15}Pb_4$ is cubic [Pearson3]. In later, more careful work [75Mul], it was found that two phases were sometimes formed in the preparation of $Na_{15}Sn_4$. The orthorhombic phase was given a "corrected" stoichiometry $Na_{3.7}Sn$ (compare $Na_{3.75}Sn = Na_{15}Sn_4$). In the orthorhombic phase, the Sn atoms are isolated with respect to each other, each having 11 Na atoms as nearest neighbors; these Na atoms form distorted pentagons and trigonal prisms around the Sn atoms [75Mul]. The packing of the atoms is less dense than in $Na_{15}Pb_4$. The same authors in a later investigation [78Mul] identified the exact stoichiometry $Na_{15}Sn_4$ with a cubic structure, the same type as $Na_{15}Pb_4$. The question arises [78Mul] whether the orthorhombic and cubic structures are different structures of the same molecular species. Diffraction patterns of both structures were recorded with a high-temperature camera up to the melting point: no transformation was observed [78Mul]. For this reason, both structures are included in Tables 3 and 4.

Na_9Sn_4 is orthorhombic, isostructural with Li_9Ge_4 [78Mul]. The low-temperature form of NaSn is tetragonal, isotypic with NaPb. In this structure, Sn_4^{4-} groups are tetrahedral, isoelectronic with P_4 [77Mul].

Thermodynamics

The excess chemical potential of Na in liquid Na-Sn solution was determined by emf measurements in several studies [49Hau, 54Del, 59Mor, 69Yua, 72Hub, 76Mai, 78Riv, 82Rai, 82Tam, 83Alq, 84Sab, 85Iwa]. The combined data cover the entire composition range and 250 to 850 °C. The enthalpy of mixing was measured by direct calorimetry at 500 °C [61Kle] and 607 °C [52Mck]. Representative data for the enthalpy of mixing at 500 °C are plotted in Fig. 2. The pronounced minimum near 45 at.% Sn appears also at higher and lower temperatures [52Mck, 82Tam] and suggests strong interaction in the liquid; this is corroborated by neutron diffraction measurements [83Alb]. The enthalpy of formation of some Na-Sn compounds was determined by direct calorimetry at 25 °C [38Kub, 56Kub] and by solution calorimetry at the same temperature [24Bil, 37Bil]. Better results were obtained by direct high-temperature calorimetry [52Mck], and these authors [52Mck] also present a compilation of all earlier data. The re-

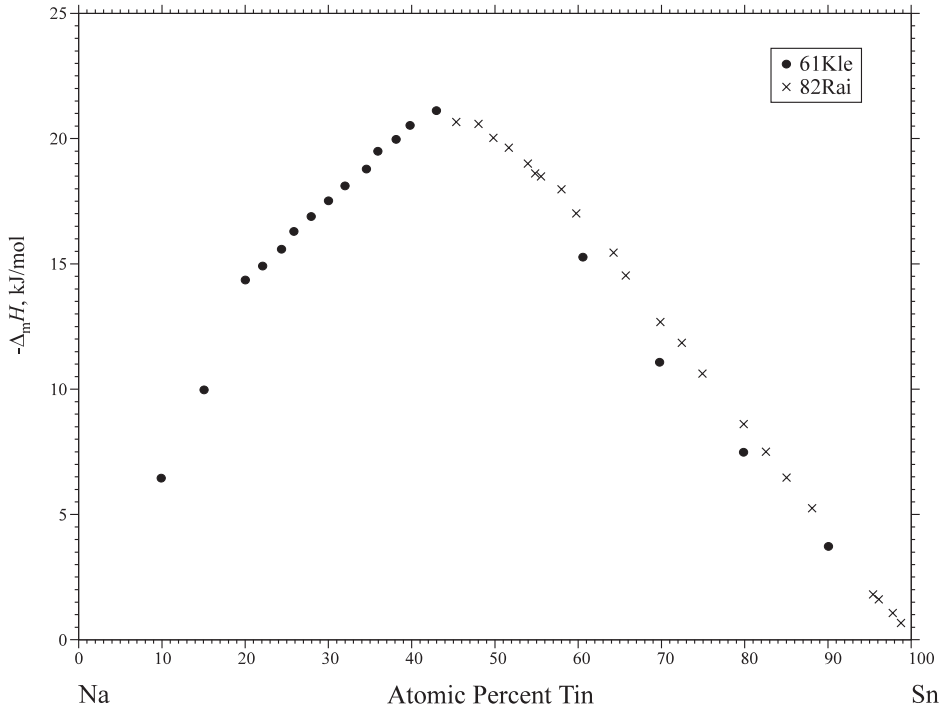

Fig. 2 Enthalpy of mixing of Na-Sn solutions at 500 °C.

cent values for NaSn [69Yua] fall within the range of uncertainty of previous determinations.

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# Indicates presence of a phase diagram.

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