The Cs-Sn (Cesium-Tin) System

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Equilibrium Diagram

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

The assessed phase diagram was constructed from the combined results of two independent studies [79Dri, 81Dri] and [82Yat, 87Mel]. The liquidus data in both studies were given only as points on phase diagrams, from which they were read. Both groups performed thermal analyses on alloys in sealed containers, either of stainless steel [79Dri, 81Dri] or Mo [82Yat, 87Mel]. In the more recent work [82Yat, 87Mel], the boundary of the two-liquid phase region was defined through "thermomagnetic analysis" and "solubility" measurements.

There are two eutectics in this system, the temperatures of both of which are indistinguishable from the melting points of the pure elements. The eutectic compositions were assumed to be almost identical to the pure components (a liquid alloy of 99.5 at.% Sn showed a thermal arrest at the eutectic temperature, ~28 ° C), and zero solid solubility [87Mel] was implied. In the absence of any more specific information, these assumptions are incorporated in Fig. 1.

The monotectic temperature was reported to be 605 °C [79Dri, 81Dri] or 590 °C [87Mel, 82Yat]. The miscibility gap at the monotectic temperature is according to [79Dri, 81Dri], 7.5 to 39 at.% Sn as stated in the text. However, on their phase diagrams [79Dri, 81Dri] the range is 10 to 39 at.% Sn. The boundaries of the two-phase liquid region were better defined by [82Yat, 87Mel] to be 2.3 to 39 at.% Sn, and the critical point is 760 °C, 20 at.% Sn [82Yat, 87Mel].

According to [79Dri, 81Dri], thermal arrests at 565 °C observed in the range 10 to 50 at.% Sn were attributable to Cs_2Sn. No such thermal phenomenon was observed in the later work [82Yat, 87Mel], in which attempts were made to isolate a Cs-rich compound from alloys of 10, 20, and 40 at.% Sn, chemical analysis revealed only Cs and CsSn. The absence of Cs-rich compounds was corroborated by [79Str].

CsSn was prepared by direct reaction between the elements [64Hew, 79Dri, 79Str, 81Dri, 82Yat, 87Mel] and was characterized by its x-ray powder diffraction pattern [64Hew, 87Mel]. According to [79Dri, 81Dri], this compound melts incongruently at 630 °C, showing a peritectic composition of 41 at.% Sn. Later work [82Yat, 87Mel], claims that CsSn melts congruently at 884 °C, with a solid transition at 630 °C. In the proposed phase diagram [82Yat, 87Mel] however, the presence of a congruently melting CsSn implies the presence also of a high-temperature eutectic. The published diagram [87Mel] shows thermal arrests that may correspond to this eutectic, but there is no mention of this in the text. Further, although the Li-Sn and Na-Sn systems both contain congruently melting one-to-one compounds, the corresponding compounds in both the K-Sn and Rb-Sn systems melt incongruently. The assessed Cs-Sn phase diagram shows a peritectic for CsSn in conformity with the other heavy alkali metal + Sn systems.

Cs_2Sn_3 was prepared by direct reaction of the elements [79Dri, 81Dri, 82Yat, 84Dri, 87Mel]. It melts congruently, and its melting point is the highest temperature on the Cs-Sn liquidus: 930 °C [79Dri, 81Dri] or 935 °C [82Yat, 87Mel]. The compound was characterized by its powder x-ray [79Dri, 84Dri] and neutron [84Dri] diffraction patterns.

The compound $CsSn_2$ melts incongruently at 875 °C [79Dri, 81Dri, 82Yat, 87Mel], with a liquid composition of 76.5 at.% Sn [79Dri, 81Dri] at the peritectic temperature.

The most Sn-rich compound in this system melts incongruently at 580 °C [79Dri, 81Dri, 82Yat, 87Mel]. It was as-

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

Reaction	Composition of the respective phases, at.% Sn			Temperature, °C	Reaction type
L ↔ (Cs)		0		28.39	Melting
L ↔ (Cs) + CsSn	~0	0	50.0	~28	Eutectic
L ↔ L + CsSn	2.3	40	50.0	600	Monotectic
(Cs,Sn) ↔ (Cs) + (Sn)		20.0		760	Critical
L + Cs_2Sn_3 ↔ CsSn	40.5	60.0	50.0	630	Peritectic
L ↔ Cs_2Sn_3			60.0	930	Congruent
L + Cs_2Sn_3 ↔ $CsSn_2$	76.5	60.0	66.7	875	Peritectic
L + $CsSn_2$ ↔ Cs_8Sn_{46}	97.5	66.7	85.2	580	Peritectic
L ↔ Cs_8Sn_{46} + (Sn)	~100	85.2	100	~232	Eutectic
L ↔ (βSn)		100		231.9681	Melting

signed the stoichiometry $CsSn_4$ [79Dri, 81Dri] or $CsSn_6$ [82Yat], but was later identified [87Mel] as Cs_8Sn_{46} from its powder XRD pattern. The authors [87Mel] make this assignment by analogy with K_8Sn_{46} in the K-Sn system. (There may be a corresponding compound in the Rb-Sn system also, but this has not yet been established.)

Crystal Structures and Lattice Parameters

The crystal structure and lattice parameter data are summarized in Table 2. CsSn is body-centered tetragonal and is isostructural with KSn and RbSn [64Hew]. From powder x-ray

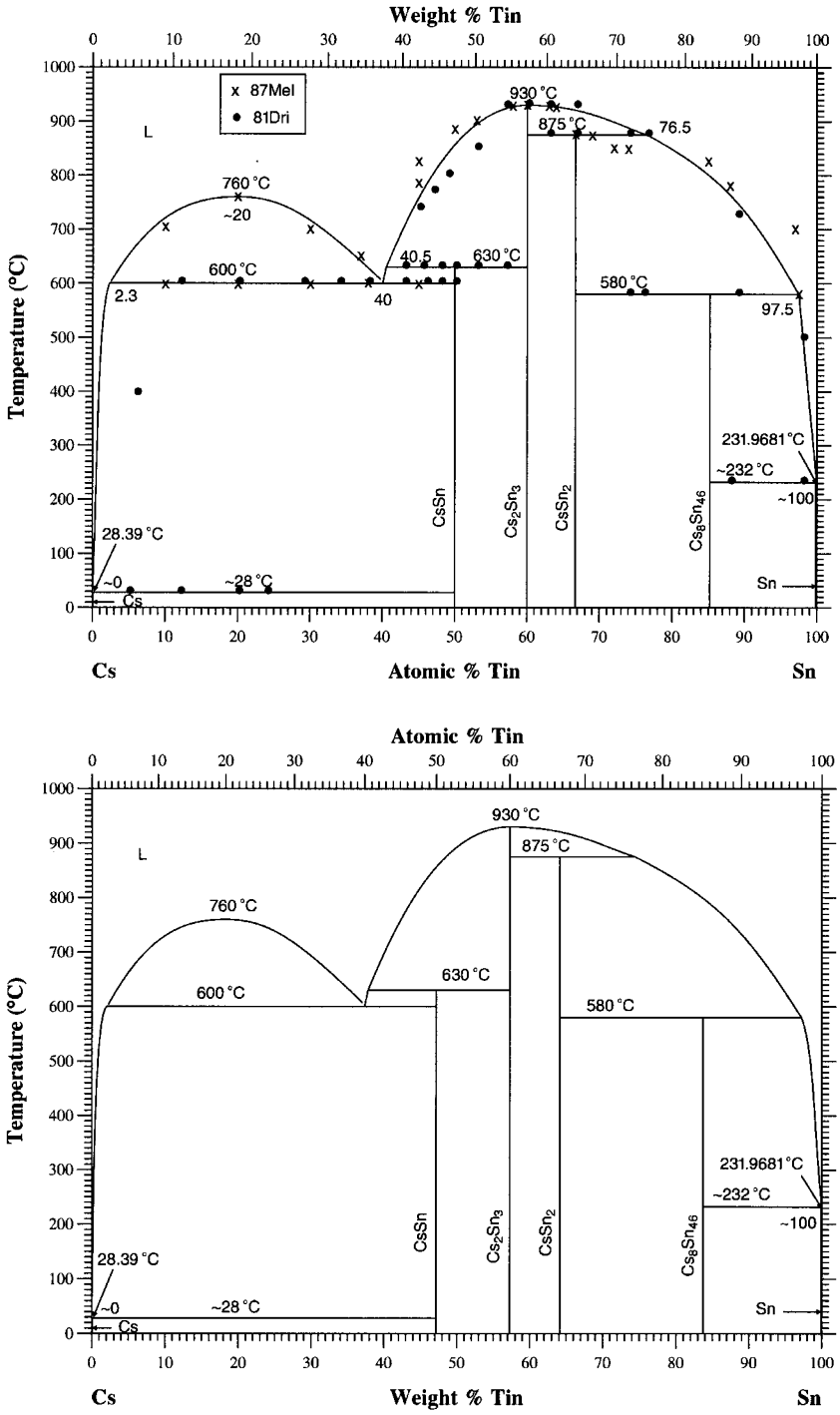

Fig. 1 Assessed Cs-Sn phase diagram.

Table 2 Cs-Sn Crystal Structure and Lattice Parameter Data at 25 °C

Phase	Composition, at.% Sn	Pearson symbol	Space group	Strukturbericht designation	Prototype	Lattice parameters, nm *a*	*c*	Reference
(Cs)	0	*cI*2	$Im\bar{3}m$	*A*2	W	0.6141	…	[Massalski2]
CsSn	50.0	*tI*64	$I4_1/acd$	…	NaPb	1.219	1.987	[64Hew]
						1.206	1.965	[87Mel]
Cs_2Sn_3	60.0	*tP*	*P*4/*mcc* or *P*4/*cc*(a)	…	…	0.760	1.368	[84Dri]
Cs_8Sn_{46}	85.2	*cP*54	$Pm\bar{3}n$	…	K_4Sn_{23}	1.2096	…	[87Mel]
(αSn)(b)	100	*cF*8	$Fd\bar{3}m$	*A*4	C(d)	0.64892	…	[Massalski2]
(βSn)	100	*tI*4	$I4_1/amd$	*A*5	βSn	0.58318	0.31818	[Massalski2]

(a) Not currently resolvable (see text). **(b)** *<18 °C.*

and neutron diffraction data [79Dri, 84Dri], Cs_2Sn_3 is tetragonal with space group *P*4/*mcc* or *P*4/*cc*. In the Cs_8Sn_{46} structure [87Mel], similar to gas hydrates (or clathrates) $8X46H_2O$, the Sn atoms form "cages" of pentagonal dodecahedrons for the Cs guest atoms [69Gal].

Thermodynamics

The vapor pressure of Cs over CsSn [79Str], Cs_2Sn_3 [80Dri], and a Cs + CsSn mixture [80Vor] were measured in the temperature ranges 247 to 427 °C, 274 to 364 °C, and 63 to 345 °C, respectively. From the vapor pressure-temperature relations for the pure compounds, it was possible to deduce standard enthapies of formation: –86.8 kJ/g-atom for CsSn [79Str] and –113 kJ/g-atom for Cs_2Sn_3 [80Dri].

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# Indicates presence of a phase diagram.

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