The K-Sn (Potassium-Tin) System

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Equilibrium Diagram

The assessed K-Sn phase diagram is shown in Fig. 1. The special points of the diagram are listed in Table 1.

Phase diagram data were obtained by thermal analysis [08Smi, 81Dri]. The earlier investigator [08Smi] reported considerable experimental difficulty, due primarily to the high volatility of K at the liquidus temperatures (boiling point of K = 774 °C). The data of the later investigators [81Dri] were only presented as points on a phase diagram, from which they were read. Although there are few experimental details given in the later work [81Dri], the assessed phase diagram has been drawn in accordance with these results [81Dri], assumed here to be more reliable. In particular, [81Dri] shows a rather flat liquidus in the range 20 to 40 at.% Sn, suggesting incipient liquid-liquid phase separation that is also observed in the Rb-Sn and Cs-Sn systems [81Dri].

Both reports [08Smi, 81Dri] indicate two eutectics in this system, the temperatures of which were indistinguishable from the melting points of the elements. There are no data on solid solubilities nor on the eutectic compositions; eutectic arrests were observed [08Smi] only as low as 5 and as high as 97 at.% Sn. In the absence of any specific information, it is reasonable to assume that there is zero solid solubility at both extremes and that the eutectic compositions are almost identical with the pure elements. The remaining features of the phase diagram are discussed with reference to intermetallic compounds.

The possible existence of "K_4Sn" was suggested [80Guk] on the basis of limited XRD data. If this compound were present in the phase diagram, it would probably melt incongruently somewhere in the interval 63 to 535 °C, but no peritectic arrests were observed [08Smi, 81Dri].

K_2Sn was identified [08Smi, 81Dri] as the species corresponding to a peritectic at 535 °C. The peritectic composition is approximately 20 at.% Sn [08Smi, 81Dri]. Limited x-ray data [80Guk] as well as emf measurements [21Kre] corroborate the existence of this compound.

KSn was prepared by direct reaction of the elements [64Hew, 81Dri]. It was characterized by its single-crystal XRD pattern [64Hew]. According to recent results [81Dri], KSn melts incongruently at 740 °C, peritectic composition about 49 at.% Sn. In the older work [08Smi] thermal arrests were observed at 670 °C, which were thought [08Smi] to correspond either to KSn peritectic melting or KSn solid transformation. This phenomenon was not reported in the later work [81Dri].

K_2Sn_3 was prepared from the elements [08Smi, 81Dri], although in the earlier work [08Smi] it was identified mainly as an alloy of 60 at.% Sn. Its congruent melting point is the highest temperature on the K-Sn liquidus, reported as 824 °C [08Smi], 830 °C [64Hew], or 860 °C [81Dri]. The compound is not mentioned, however, in the emf [21Kre] or x-ray [80Guk] investigations.

The existence of KSn_2 was inferred from the early thermal analysis results [08Smi]. A compound of this stoichiometry was prepared in liquid ammonia [26Ber], and its existence was corroborated by the emf [21Kre] and x-ray [80Guk] investigations. It melts incongruently at 710 °C [81Dri] at a peritectic liquid composition of about 83.5 at.% Sn.

"KSn_4" was thought to be the most Sn-rich compound [08Smi, 21Kre, 80Guk, 81Dri]. It was shown to be more correctly K_8Sn_{46} from its single-crystal XRD pattern [69Gal]. It melts incongruently at 600 °C at a peritectic liquid composition of approximately 90.5 at.% Sn [08Smi, 81Dri]. Thermal arrests were observed [08Smi] at 414 °C and were ascribed to a solid

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

Reaction	Composition of the respective phases, at.% Sn			Temperature, °C	Reaction type
L ↔ (K)		0		63.71	Melting point
L ↔ (K) + K_2Sn	~0	0	33.3	~63	Eutectic
L + KSn ↔ K_2Sn	20.5	50.0	33.3	535	Peritectic
L + K_2Sn_3 ↔ KSn	49.0	60.0	50.0	740	Peritectic
L ↔ K_2Sn_3		60.0		860	Congruent point
L + K_2Sn_3 ↔ KSn_2	83.5	60.0	66.7	710	Peritectic
L + KSn_2 ↔ K_8Sn_{46}	90.5	66.7	85.2	600	Peritectic
L ↔ K_8Sn_{46} + (Sn)	~100	85.2	100	~232	Eutectic
L ↔ (βSn)		100		231.9681	Melting point

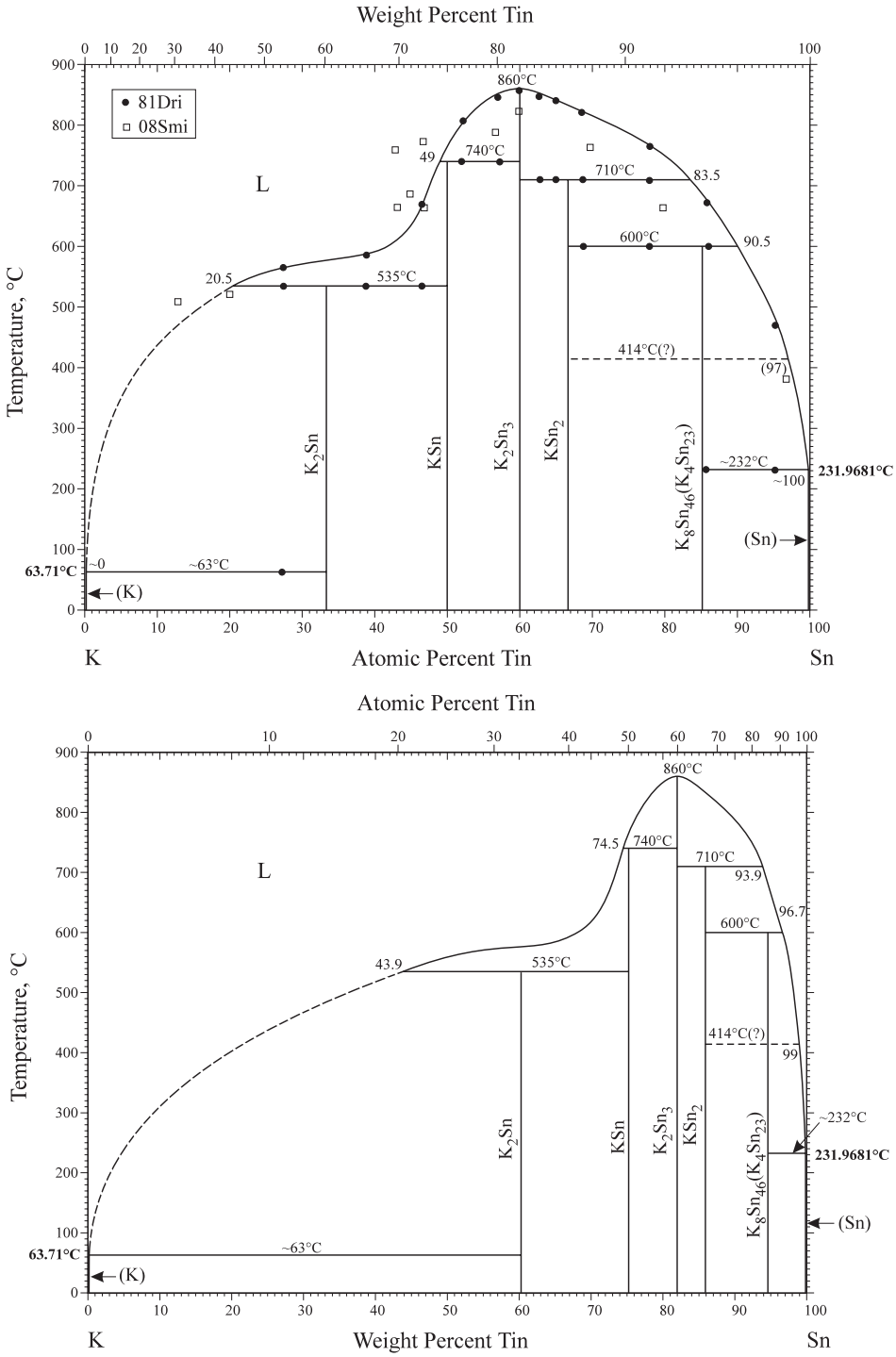

Fig. 1 Assessed K-Sn phase diagram.

transformation of "KSn_4" [08Smi], although this thermal phenomenon was not reported in later work [81Dri].

There is no report of any detectable homogeneity range of any of the compounds, and so they are assumed to be stoichiometric.

Crystal Structures and Lattice Parameters

The crystal data are summarized in Table 2. KSn is isostructural with NaPb [64Hew], that is, body-centered tetragonal with

Table 2 K-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
(K)	0	*cI*2	$Im\bar{3}m$	*A*2	W	0.5321	…	[Massalski2]
KSn	50	*tI*64	$I4_1/acd$	…	NaPb	1.142	1.857	[64Hew]
K_8Sn_{46}(a)	85.2	*cP*54	$Pm\bar{3}n$	…	K_4Si_{23}	1.203	…	[69Gal]
(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) In [Pearson3] this is indicated K_4Sn_{23}. **(b)** <18 °C.

Sn_4 tetrahedral groups. K_8Sn_{46} (or K_4Sn_{23} according to [Pearson3]) is isostructural with K_8Si_{46} and K_8Ge_{46} [69Gal], the overall symmetry being cubic. The structure of K_8Sn_{46} is analogous to hydrates (or clathrates) $8X.46H_2O$, where the water molecules form "cages" for the guest *X* molecules. The Sn atoms take the place of the water molecules and are arranged in pentagonal dodecahedrons [69Gal].

Thermodynamics

The excess chemical potential of K in liquid K-Sn solution was deduced from emf measurements in the range 500 to 580 °C and compositions ≥90.5 at.% Sn [72Byk]. The derived excess enthalpy and excess Gibbs energies are strongly negative, which suggests high ordering in the liquid state. This is consistent with the existence of the intermetallic compounds.

Cited References

08Smi: D.P. Smith, "Alloys of K with Al, Mg, Zn, Cd, Bi, Sn and Pb," *Z. Anorg. Chem.*, *56*(1), 109-142 (1908) in German. (Equi Diagram; Experimental; #)

21Kre: R. Kremann and E. Pressfreund, "The Electromotive Behavior of Some Binary Alloys XV. Alloys of K with Pb, Sn and Tl and of Na with Sb," *Z. Metallkde.*, *13*, 19-29 (1921) in German. (Equi Diagram;Experimental)

26Ber: F.W. Bergstrom, "The Action of Solutions of Ammono Bases in Liquid Ammonia on Elements More Electronegative than Ni," *J. Phys. Chem.*, *30*(1), 12-19 (1926). (Equi Diagram; Experimental)

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69Gal: J. Gallmeir, H. Schäfer, and A. Weiss, "Cage Structure as a Common Building Principle of Compounds K_8E_{46} (*E* = Si, Ge, Sn)," *Z. Naturforsch. B*, *24*(6), 665-667 (1969) in German. (Equi Diagram, Crys Structure; Experimental)

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81Dri: M.E. Drits, A.S. Fridman, L.L. Zusman, and V.A. Kusikov, "Phase Diagram of Sn with K, Rb and Cs," *Fazovye Ravnovesiya Met. Splavakh*, 176-178 (1981) in Russian. (Equi Diagram; Experimental; #)

# Indicates presence of a phase diagram.

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