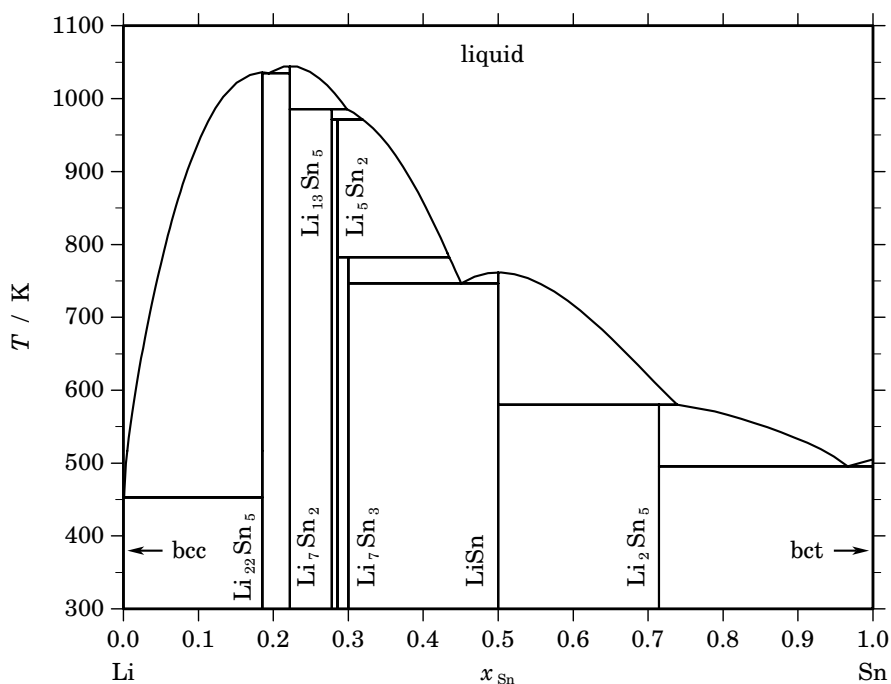


Li – Sn (Lithium – Tin)**Fig. 1.** Calculated phase diagram for the system Li-Sn.

Tin based materials are promising candidates for replacing conventional graphite anodes in Li-ion batteries. Compared with the intercalation compound LiC_6 which is formed with graphite the intermetallic lithium tin compounds can reach much higher storage capacities of Li per mass, especially in $\text{Li}_{22}\text{Sn}_5$. The literature on the Li-Sn system has been reviewed in [1998San] and a thermodynamic dataset has been optimised by [2005Yin]. The assessment is based on literature data on the phase diagram and on thermodynamic measurements. The selected phase equilibria have been reported by [1910Mas, 1932Bar, 1934Gru, 1964Fos, 1979Bai, 1982Dad]. Enthalpies of formation in the liquid and in two-phase regions with intermetallic compounds have been investigated at several temperatures in [1986Mos]. The activities of Li in the liquid have been measured at 1473 K by [1972Fis] and activities of Sn at 688 K have been reported in [1981Wen]. For their assessment [2005Yin] have selected enthalpies and entropies of formation for the intermetallic compounds at 688 K reported by [1981Wen] and enthalpies of formation at 298 K which have been given in [1938Kub].

Table I. Phases, structures and models.

Phase	Struktur- bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	(Li,Sn) ₁
bcc	A2	W	<i>cI2</i>	<i>Im$\bar{3}m$</i>	BCC_A2	(Li,Sn) ₁
Li ₂₂ Sn ₅	<i>cF432</i>	<i>F23</i>	LI22SN5	Li ₂₂ Sn ₅
Li ₇ Sn ₂	<i>oC36</i>	<i>Cmmm</i>	LI7SN2	Li ₇ Sn ₂
Li ₁₃ Sn ₅	<i>hP18</i>	<i>P$\bar{3}m1$</i>	LI13SN5	Li ₁₃ Sn ₅
Li ₅ Sn ₂	D8 _i	Mo ₂ B ₅	<i>hR7</i>	<i>R$\bar{3}m$</i>	LI5SN2	Li ₅ Sn ₂
Li ₇ Sn ₃	<i>mP20</i>	<i>P2₁/m</i>	LI7SN3	Li ₇ Sn ₃
LiSn	<i>mP6</i>	<i>P2/m</i>	LISN	Li ₁ Sn ₁
Li ₂ Sn ₅	<i>tI14</i>	<i>P4/mbm</i>	LI2SN5	Li ₂ Sn ₅
bct	A5	β Sn	<i>tI4</i>	<i>I4₁/amd</i>	BCT_A5	Sn ₁

Table II. Invariant reactions.

Reaction	Type	<i>T</i> / K	Compositions / <i>x</i> _{Sn}			$\Delta_r H$ / (J/mol)
liquid \rightleftharpoons Li ₇ Sn ₂	congruent	1044.9	0.222	0.222		−20155
liquid \rightleftharpoons Li ₂₂ Sn ₅	congruent	1035.9	0.185	0.185		−24056
liquid \rightleftharpoons Li ₂₂ Sn ₅ + Li ₇ Sn ₂	eutectic	1035.0	0.194	0.185	0.222	−23048
Li ₇ Sn ₂ + liquid \rightleftharpoons Li ₁₃ Sn ₅	peritectic	985.6	0.222	0.298	0.278	−10830
Li ₁₃ Sn ₅ + liquid \rightleftharpoons Li ₅ Sn ₂	peritectic	971.5	0.278	0.319	0.286	−2660
Li ₅ Sn ₂ + liquid \rightleftharpoons Li ₇ Sn ₃	peritectic	782.6	0.286	0.435	0.300	−1213
liquid \rightleftharpoons LiSn	congruent	761.5	0.500	0.500		−13741
liquid \rightleftharpoons Li ₇ Sn ₃ + LiSn	eutectic	746.7	0.451	0.300	0.500	−12967
LiSn + liquid \rightleftharpoons Li ₂ Sn ₅	peritectic	580.0	0.500	0.739	0.714	−10446
liquid \rightleftharpoons Li ₂ Sn ₅ + bct	eutectic	495.7	0.966	0.714	1.000	−8065
liquid \rightleftharpoons bcc + Li ₂₂ Sn ₅	eutectic	453.1	0.001	0.000	0.185	−3049

Table IIIa. Integral quantities for the liquid phase at 1100 K.

<i>x</i> _{Sn}	ΔG_m [J/mol]	ΔH_m [J/mol]	ΔS_m [J/(mol·K)]	G_m^E [J/mol]	S_m^E [J/(mol·K)]	ΔC_P [J/(mol·K)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−17271	−14783	2.262	−14298	−0.441	0.000
0.200	−27280	−24058	2.929	−22703	−1.231	0.000
0.300	−32274	−28656	3.290	−26687	−1.789	0.000
0.400	−33618	−29410	3.826	−27463	−1.770	0.000
0.500	−32323	−27154	4.700	−25984	−1.064	0.000
0.600	−29100	−22723	5.797	−22945	0.201	0.000
0.700	−24367	−16954	6.739	−18780	1.660	0.000
0.800	−18243	−10684	6.872	−13667	2.711	0.000
0.900	−10494	−4753	5.219	−7521	2.516	0.000
1.000	0	0	0.000	0	0.000	0.000

Reference states: Li(liquid), Sn(liquid)

Table IIIb. Partial quantities for Li in the liquid phase at 1100 K.

x_{Li}	ΔG_{Li} [J/mol]	ΔH_{Li} [J/mol]	ΔS_{Li} [J/(mol·K)]	G_{Li}^{E} [J/mol]	S_{Li}^{E} [J/(mol·K)]	a_{Li}	γ_{Li}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−4177	−2893	1.168	−3213	0.292	0.633	0.704
0.800	−12803	−10462	2.128	−10762	0.272	0.247	0.308
0.700	−23352	−21044	2.098	−20089	−0.868	0.078	0.111
0.600	−34091	−32970	1.019	−29419	−3.228	0.024	0.040
0.500	−44090	−44567	−0.433	−37751	−6.196	0.008	0.016
0.400	−53242	−54159	−0.834	−44862	−8.452	0.003	0.007
0.300	−62319	−60068	2.047	−51308	−7.964	0.001	0.004
0.200	−73141	−60608	11.393	−58421	−1.989	0.000	0.002
0.100	−89371	−54094	32.070	−68312	12.925	0.000	0.001
0.000	−∞	−38833	∞	−83868	40.941	0.000	0.000

Reference state: Li(liquid)

Table IIIc. Partial quantities for Sn in the liquid phase at 1100 K.

x_{Sn}	ΔG_{Sn} [J/mol]	ΔH_{Sn} [J/mol]	ΔS_{Sn} [J/(mol·K)]	G_{Sn}^{E} [J/mol]	S_{Sn}^{E} [J/(mol·K)]	a_{Sn}	γ_{Sn}
0.000	−∞	−178137	∞	−178002	−0.123	0.000	0.000
0.100	−135120	−121795	12.113	−114061	−7.032	0.000	0.000
0.200	−85190	−78439	6.137	−70470	−7.245	0.000	0.000
0.300	−53094	−46416	6.071	−42083	−3.939	0.003	0.010
0.400	−32909	−24070	8.036	−24529	0.417	0.027	0.068
0.500	−20557	−9741	9.833	−14217	4.069	0.106	0.211
0.600	−13005	−1766	10.218	−8333	5.970	0.241	0.402
0.700	−8102	1523	8.750	−4840	5.785	0.412	0.589
0.800	−4519	1797	5.741	−2478	3.886	0.610	0.763
0.900	−1730	729	2.235	−766	1.359	0.828	0.920
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Sn(liquid)

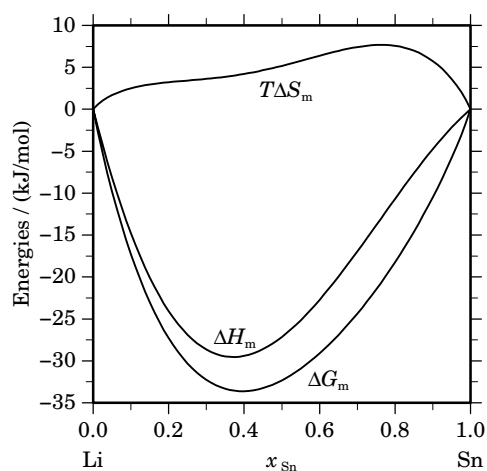
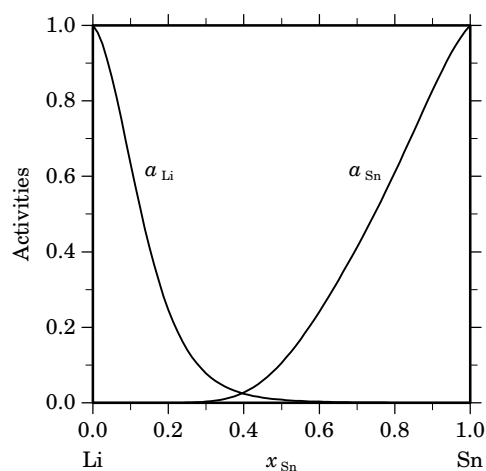
**Fig. 2.** Integral quantities of the liquid phase at $T=1100$ K.**Fig. 3.** Activities in the liquid phase at $T=1100$ K.

Table IV. Standard reaction quantities at 298.15 K for the compounds per mole of atoms.

Compound	x_{Sn}	$\Delta_f G^\circ / (\text{J/mol})$	$\Delta_f H^\circ / (\text{J/mol})$	$\Delta_f S^\circ / (\text{J}/(\text{mol}\cdot\text{K}))$	$\Delta_f C_P^\circ / (\text{J}/(\text{mol}\cdot\text{K}))$
$\text{Li}_{22}\text{Sn}_5$	0.185	–39617	–43314	–12.399	0.000
Li_7Sn_2	0.222	–39321	–41722	–8.051	0.000
$\text{Li}_{13}\text{Sn}_5$	0.278	–38604	–39897	–4.335	0.000
Li_5Sn_2	0.286	–38497	–39652	–3.875	0.000
Li_7Sn_3	0.300	–38272	–39382	–3.725	0.000
Li_1Sn_1	0.500	–34974	–35905	–3.123	0.000
Li_2Sn_5	0.714	–21424	–21834	–1.375	0.000

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