

Se – Tl (Selenium – Thallium)

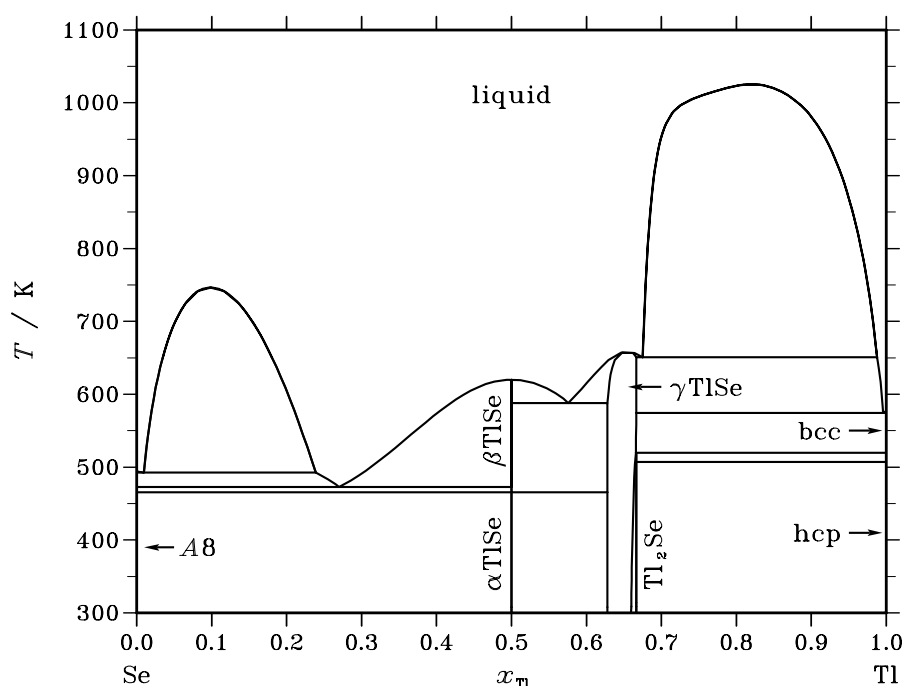


Fig. 1. Calculated phase diagram for the system Se-Tl.

The Se-Tl system has been investigated and assessed by [00Rom]. Three intermediate compounds exist in the system: TlSe with two stoichiometric polymorphic forms α (low temperature) and β (high temperature) which melts congruently at 620 K, Tl_2Se which decomposes into bcc-Tl and γTlSe at 520 K. The γTlSe phase is non-stoichiometric and extends from $x_{\text{Se}}=0.336$ to $x_{\text{Se}}=0.373$ and it melts congruently at 657.8 K. Two monotectic reactions are present in the system which generate two liquid-liquid miscibility gaps, one on the Tl-rich side and another one on the Se-rich side. The phase diagram has been established with experimental data of DTA, DSC, X-ray, thermodynamic data of heat content and C_p for TlSe and γTlSe and enthalpies of mixing in the liquid. The chemical potential of Tl was determined in the liquid state by EMF and vapour pressure measurements. The comparison between the experimental data and the calculated phase diagram shows very good agreement.

Table I. Phases, structures and models.

Phase	Strukturbericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(\text{Se}, \text{Tl}_2\text{Se}, \text{Tl})_1$
A8	A8	γSe	$hP3$	$P3_121$	TRIGONAL_A8	Se_1
αTlSe	TLSE_LOW	Tl_1Se_1
βTlSe	B37	TlSe	$tI16$	$I4/mcm$	B37_TLSE	Tl_1Se_1
γTlSe	$tP32$	$P4/ncc$	TL5SE3	$\text{Tl}_5\text{Se}_2(\text{Se}, \text{Tl})_1$
Tl_2Se	TL2SE	Tl_2Se_1
bcc	A2	W	$cI2$	$Im\bar{3}m$	BCC_A2	Tl_1
hcp	A3	Mg	$hP2$	$P6_3/mmc$	HCP_A3	Tl_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Tl}			$\Delta_r H / (\text{J/mol})$
liquid \rightleftharpoons liquid'' + liquid'''	critical	1025.4	0.821	0.821	0.821	0
liquid \rightleftharpoons liquid' + liquid''	critical	746.0	0.100	0.100	0.100	0
liquid \rightleftharpoons γ TlSe	congruent	657.8	0.654	0.654		–6079
liquid'' \rightleftharpoons γ TlSe + liquid'''	monotectic	650.7	0.675	0.667	0.988	–5433
liquid'' \rightleftharpoons β TlSe	congruent	620.3	0.500	0.500		–11175
liquid'' \rightleftharpoons β TlSe + γ TlSe	eutectic	588.0	0.576	0.500	0.628	–8679
liquid''' \rightleftharpoons γ TlSe + bcc	eutectic	574.3	0.996	0.667	1.000	–4259
γ TlSe + bcc \rightleftharpoons Tl ₂ Se	peritectoid	519.8	0.666	1.000	0.667	–166
Tl ₂ Se + bcc \rightleftharpoons hcp	degenerate	507.0	0.667	1.000	1.000	–360
liquid' \rightleftharpoons A8 + liquid''	monotectic	492.7	0.010	0.000	0.239	–5967
liquid'' \rightleftharpoons A8 + β TlSe	eutectic	472.7	0.270	0.000	0.500	–8302
β TlSe \rightleftharpoons α TlSe	polymorphic	465.7	0.500	0.500		–138

Table IIIa. Integral quantities for the stable phases at 738 K.

Phase	x_{Tl}	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)]
liquid''	0.000	0	0	0.000	0	0.000	0.000
	0.100	–7096	–4861	3.028	–5101	0.325	0.006
	0.200	–14064	–10305	5.094	–10994	0.934	0.004
	0.300	–20735	–16001	6.414	–16987	1.335	0.003
	0.400	–26492	–21458	6.820	–22362	1.225	0.004
	0.500	–30567	–26207	5.907	–26314	0.144	0.010
	0.600	–32411	–30383	2.748	–28281	–2.848	0.033
	0.678	–29296	–29804	–0.689	–25442	–5.911	2.042
liquid'''	0.977	–2195	–1638	0.755	–1527	–0.151	0.001
	1.000	0	0	0.000	0	0.000	0.000

Reference states: Se(liquid), Tl(liquid)

Table IIIb. Partial quantities for Se in the stable phases at 738 K.

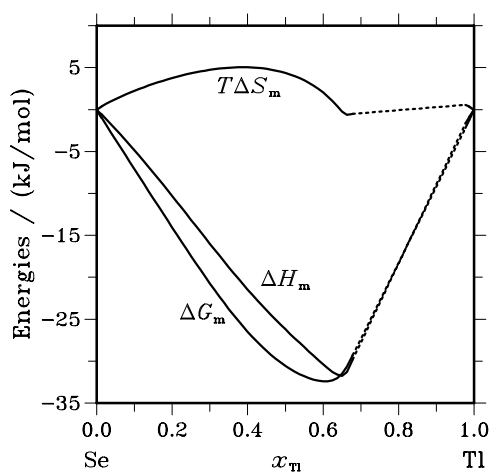
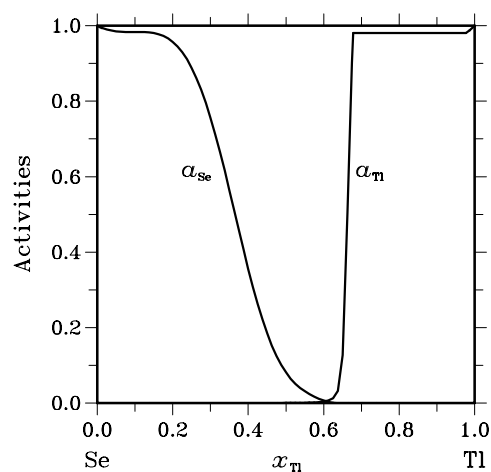
Phase	x_{Se}	ΔG_{Se} [J/mol]	ΔH_{Se} [J/mol]	ΔS_{Se} [J/(mol·K)]	G_{Se}^{E} [J/mol]	S_{Se}^{E} [J/(mol·K)]	a_{Se}	γ_{Se}
liquid''	1.000	0	0	0.000	0	0.000	1.000	1.000
	0.900	–104	331	0.590	543	–0.286	0.983	1.092
	0.800	–270	974	1.685	1100	–0.170	0.957	1.196
	0.700	–1718	1007	3.693	471	0.727	0.756	1.080
	0.600	–6341	–840	7.453	–3206	3.206	0.356	0.593
	0.500	–15409	–4380	14.944	–11156	9.181	0.081	0.162
	0.400	–30515	–6788	32.151	–24893	24.532	0.007	0.017
	0.322	–90857	–103102	–16.593	–83894	–26.027	0.000	0.000
liquid'''	0.023	–90857	–72827	24.430	–67669	–6.989	0.000	0.000
	0.000	– ∞	–70523	∞	–65953	–6.194	0.000	0.000

Reference state: Se(liquid)

Table IIIc. Partial quantities for Tl in the stable phases at 738 K.

Phase	x_{Tl}	ΔG_{Tl} [J/mol]	ΔH_{Tl} [J/mol]	ΔS_{Tl} [J/(mol·K)]	G_{Tl}^{E} [J/mol]	S_{Tl}^{E} [J/(mol·K)]	a_{Tl}	γ_{Tl}
liquid''	0.000	–∞	–39827	∞	–9660	–40.876	0.000	0.207
	0.100	–70026	–51597	24.971	–55897	5.826	0.000	0.000
	0.200	–69243	–55420	18.731	–59368	5.349	0.000	0.000
	0.300	–65108	–55689	12.763	–57720	2.753	0.000	0.000
	0.400	–56718	–52385	5.871	–51096	–1.747	0.000	0.000
	0.500	–45725	–48034	–3.129	–41471	–8.892	0.001	0.001
	0.600	–33675	–46114	–16.854	–30541	–21.102	0.004	0.007
	0.678	–122	4932	6.848	2258	3.623	0.980	1.445
liquid'''	0.977	–122	27	0.202	20	0.009	0.980	1.003
	1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Tl(liquid)

**Fig. 2.** Integral quantities of the stable phases at $T=738$ K.**Fig. 3.** Activities in the stable phases at $T=738$ K.**Table IV.** Standard reaction quantities at 298.15 K for the compounds per mole of atoms.

Compound	x_{Tl}	$\Delta_f G^\circ$ / (J/mol)	$\Delta_f H^\circ$ / (J/mol)	$\Delta_f S^\circ$ / (J/(mol·K))	$\Delta_f C_P^\circ$ / (J/(mol·K))
$\beta\text{Tl}_1\text{Se}_1$	0.500	–32256	–33527	–4.261	–0.968
$\alpha\text{Tl}_1\text{Se}_1$	0.500	–32305	–33662	–4.550	–0.989
Tl_2Se_1	0.667	–32988	–34599	–5.405	0.854

References

[00Rom] F. Rörmann, Y. Feutelais, S.G. Fries, R. Blachnik: Intermetallics **8** (2000) 53–65.