P – Si (Phosphorus – Silicon)

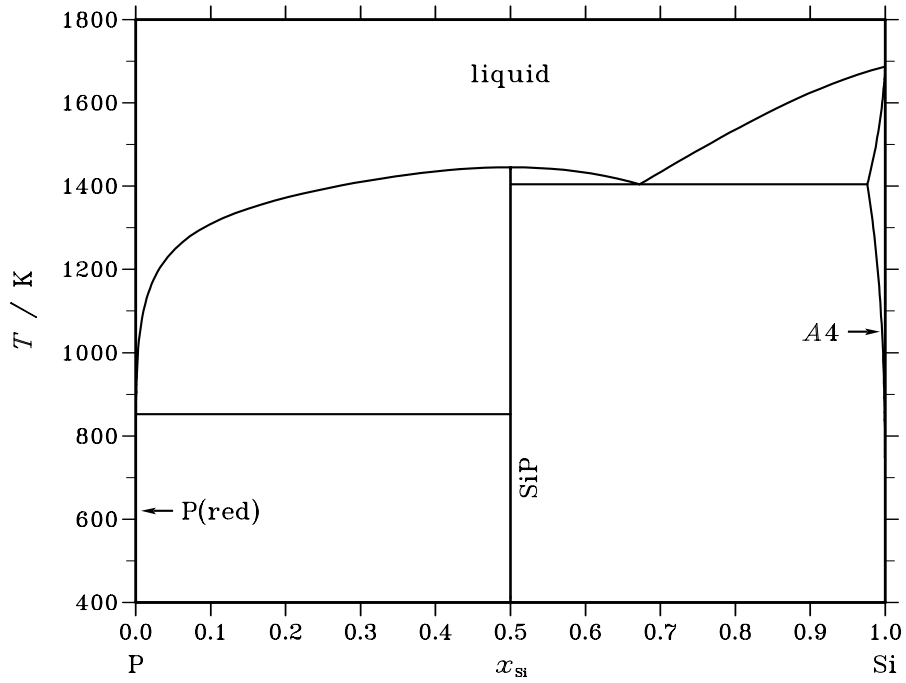

Fig. 1. Calculated phase diagram for the system P-Si (constrained system).

In spite of its importance for the purification of Si and for the electronics industry the phase diagram and thermodynamic properties of the P-Si system are still uncertain. The data have been reviewed by Olesinski *et al.* [85Ole] up to 1985. Since then further work by Ugai *et al.* [87Uga1, 87Uga2] and Miki *et al.* [96Mik] and Zaitsev *et al.* [00Zai] have shed further light. The phase diagram is characterised by the formation of a stable intermetallic compound SiP which, it is believed, dissociates at ambient pressure at about 1473 K to give a Si rich liquid phase and a P rich gas phase. Olesinski *et al.* [85Ole] report that this gas phase contains nearly 40% Si based on extrapolation of the phase boundary data from Giessen and Vogel [59Gie]. This is likely to be considerably too high in view of the extremely low vapour pressure of pure silicon at these temperatures. It is possible that the data of Giessen and Vogel were affected by oxygen contamination. There appears to be small solubility of P in solid Si up to a maximum of approximately 2.5 at.% at the eutectic temperature of approximately 1404 K. The critically assessed data adopted by SGTE for this system were assessed by Dinsdale [04Din] and are in reasonable agreement with the experimental data for the system.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(P,Si)_1$
P(red)	···	···	···	···	P_RED	P_1
αP	···	αP	$c*$*	···	P_WHITE	P_1
SiP	···	···	$oC48$	$Cmc2_1$	SIP	Si_1P_1
$A4$	$A4$	C(diamond)	$cF8$	$Fd\overline{3}m$	DIAMOND_A4	$(P,Si)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Si}			$\Delta_{\mathrm{r}}H$ / (J/mol)
liquid $\rightleftharpoons$ SiP	congruent	1445.0	0.500	0.500		−52355
liquid $\rightleftharpoons$ SiP + $A4$	eutectic	1404.0	0.672	0.500	0.976	−49385
liquid $\rightleftharpoons$ P(red) + SiP	eutectic	852.3	0.000	0.000	0.500	−18567

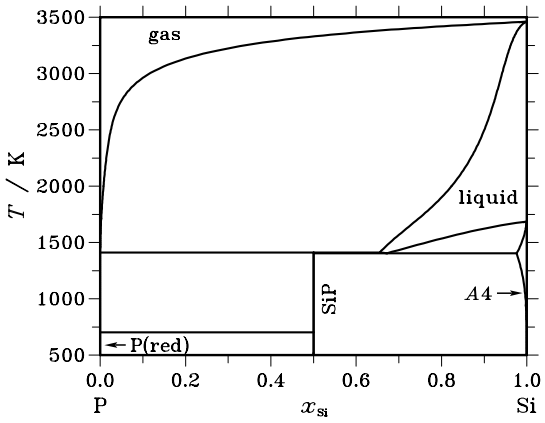

Fig. 2. Calculated phase diagram at 0.1 MPa.

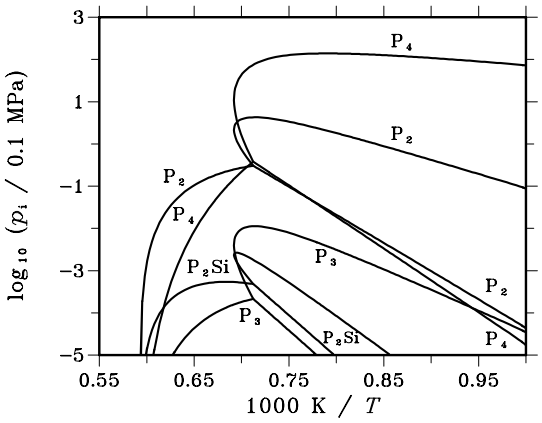

Fig. 3. Calculated partial pressures of gaseous species in the phase equilibria of the constrained system.

Table IIIa. Integral quantities for the liquid phase at 1700 K.

x_{Si}	ΔG_{m} [J/mol]	ΔH_{m} [J/mol]	ΔS_{m} [J/(mol·K)]	$G_{\mathrm{m}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{m}}^{\mathrm{E}}$ [J/(mol·K)]	ΔC_P [J/(mol·K)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−5166	−571	2.703	−571	0.000	0.000
0.200	−8496	−1423	4.161	−1423	0.000	0.000
0.300	−11039	−2405	5.079	−2405	0.000	0.000
0.400	−12875	−3362	5.596	−3362	0.000	0.000
0.500	−13939	−4141	5.763	−4141	0.000	0.000
0.600	−14102	−4589	5.596	−4589	0.000	0.000
0.700	−13187	−4552	5.079	−4552	0.000	0.000
0.800	−10951	−3878	4.161	−3878	0.000	0.000
0.900	−7006	−2411	2.703	−2411	0.000	0.000
1.000	0	0	0.000	0	0.000	0.000

Reference states: P(liquid), Si(liquid)

Table IIIb. Partial quantities for P in the liquid phase at 1700 K.

x_P	ΔG_P [J/mol]	ΔH_P [J/mol]	ΔS_P [J/(mol·K)]	G_P^E [J/mol]	S_P^E [J/(mol·K)]	a_P	γ_P
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−1323	167	0.876	167	0.000	0.911	1.012
0.800	−2692	462	1.855	462	0.000	0.827	1.033
0.700	−4462	580	2.966	580	0.000	0.729	1.042
0.600	−7008	213	4.247	213	0.000	0.609	1.015
0.500	−10743	−946	5.763	−946	0.000	0.468	0.935
0.400	−16154	−3203	7.619	−3203	0.000	0.319	0.797
0.300	−23882	−6864	10.010	−6864	0.000	0.185	0.615
0.200	−34987	−12238	13.382	−12238	0.000	0.084	0.421
0.100	−52176	−19630	19.145	−19630	0.000	0.025	0.249
0.000	−∞	−29348	∞	−29348	0.000	0.000	0.125

Reference state: P(liquid)

Table IIIc. Partial quantities for Si in the liquid phase at 1700 K.

x_{Si}	ΔG_{Si} [J/mol]	ΔH_{Si} [J/mol]	ΔS_{Si} [J/(mol·K)]	G_{Si}^E [J/mol]	S_{Si}^E [J/(mol·K)]	a_{Si}	γ_{Si}
0.000	−∞	−3783	∞	−3783	0.000	0.000	0.765
0.100	−39752	−7206	19.145	−7206	0.000	0.060	0.601
0.200	−31715	−8966	13.382	−8966	0.000	0.106	0.530
0.300	−26387	−9370	10.010	−9370	0.000	0.155	0.515
0.400	−21676	−8724	7.619	−8724	0.000	0.216	0.539
0.500	−17134	−7337	5.763	−7337	0.000	0.298	0.595
0.600	−12734	−5514	4.247	−5514	0.000	0.406	0.677
0.700	−8603	−3562	2.966	−3562	0.000	0.544	0.777
0.800	−4942	−1787	1.855	−1787	0.000	0.705	0.881
0.900	−1987	−498	0.876	−498	0.000	0.869	0.965
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Si(liquid)

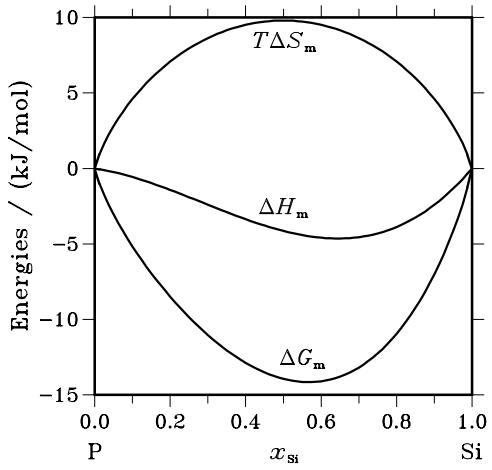

Fig. 4. Integral quantities of the liquid phase at T=1700 K.

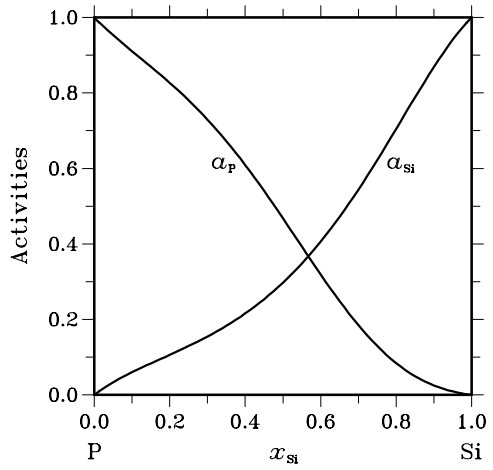

Fig. 5. Activities in the liquid phase at T=1700 K.

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

Compound	x_{Si}	$\Delta_{\mathrm{f}}G^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}H^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}S^{\circ}$ / (J/(mol·K))	$\Delta_{\mathrm{f}}C_P^{\circ}$ / (J/(mol·K))
Si_1P_1	0.500	−32798	−30559	7.508	0.000

References

[59Gie] B. Giessen, R. Vogel: Z. Metallkd. **50** (1959) 274–277.

[85Ole] R.W. Olesinski, N. Kanani: G.J. Abbaschian: Bull. Alloy Phase Diagrams **6** (1985) 130–133.

[87Uga1] Ya.A. Ugai, L.I. Sokolov, E.G. Goncharov, V.S. Makarov: Zh. Neorg. Khim. **32** (1987) 1198–1200.

[87Uga2] Ya.A. Ugai, G.V. Semenova, L.I. Sokolov, E.G. Goncharov: Zh. Neorg. Khim. **32** (1987) 1459–1462

[96Mik] T. Miki, K. Morita, N. Sano: Metall. Mater. Trans. B **27B** (1996) 937–941.

[00Zai] A.I. Zaitsev, N.E. Shelkova, A.A. Kodentsov: J. Phase Equilibria **21** (2000) 529–533.

[04Din] A.T. Dinsdale, unpublished work, 2004.