Si – V (Silicon – Vanadium)

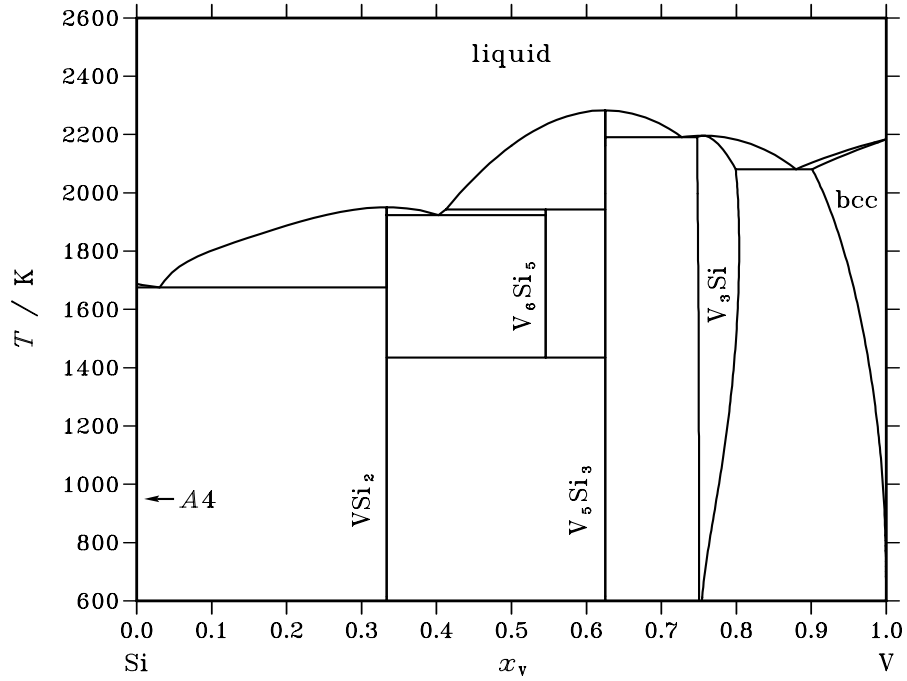

Fig. 1. Calculated phase diagram for the system Si-V.

Due to their technologically relevant characteristics, the transition metal silicides have received considerable attention in the last few decades. Silicides, in fact, find applications in catalysis, in high-temperature devices and in microelectronics, where they are commonly used for interconnects in very large scale integration (VLSI) applications. The Si-V system appears to be particularly interesting because one of the compounds present in the phase diagram, V_3Si, shows the $A15$ structure, typical of several superconducting intermetallic phases. The experimental data for the system have been reviewed by [85Smi]. A thermodynamic assessment of the Si-V system has been performed by [94Ran]. The liquid and bcc phases are described by a simple solution model, the V_3Si phase is represented by a two-sublattice model whereas VSi_2, V_5Si_3, and V_6Si_5 are treated as stoichiometric phases and $A4$ is assumed to be pure silicon. The calculated phase diagram shows significant deviations in the V-rich part from that given by [85Smi]. More recent measurements of the thermodynamic properties of the compounds [98Mes, 99Har, 00Har, 01Mes] are in fair agreement with the description of [94Ran].

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Si,V)_1$
$A4$	$A4$	C(diamond)	$cF8$	$Fd\overline{3}m$	DIAMOND_A4	Si_1
VSi_2	$C40$	$CrSi_2$	$hP9$	$P6_222$	C40_SI2V	Si_2V_1
V_6Si_5	$\cdots$	Nb_6Sn_5	$oI44$	$Immm$	SI5V6	Si_5V_6
V_5Si_3	$D8_m$	W_5Si_3	$tI32$	$I4/mcm$	D8M_SI3V5	Si_3V_5
V_3Si	$A15$	Cr_3Si	$cP8$	$Pm\overline{3}n$	A15_SIV3	$(Si,V)_1(Si,V)_3$
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Si,V)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{V}			$\Delta_{\mathrm{r}}H$ / (J/mol)
liquid $\rightleftharpoons$ V_5Si_3	congruent	2283.2	0.625	0.625		−47284
liquid $\rightleftharpoons$ V_3Si	congruent	2196.1	0.756	0.756		−43483
liquid $\rightleftharpoons$ V_5Si_3 + V_3Si	eutectic	2190.8	0.727	0.625	0.748	−43639
liquid $\rightleftharpoons$ V_3Si + bcc	eutectic	2081.1	0.879	0.799	0.901	−21634
liquid $\rightleftharpoons$ VSi_2	congruent	1950.4	0.333	0.333		−43828
liquid + V_5Si_3 $\rightleftharpoons$ V_6Si_5	peritectic	1943.1	0.413	0.625	0.545	−14867
liquid $\rightleftharpoons$ VSi_2 + V_6Si_5	eutectic	1924.0	0.403	0.333	0.545	−40911
liquid $\rightleftharpoons$ $A4$ + VSi_2	eutectic	1675.1	0.031	0.000	0.333	−49229
V_6Si_5 $\rightleftharpoons$ VSi_2 + V_5Si_3	eutectoid	1434.6	0.545	0.333	0.625	−525

Table IIIa. Integral quantities for the liquid phase at 2300 K.

x_{V}	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	−10402	−12465	−0.897	−4185	−3.600	0.000
0.200	−19089	−24240	−2.239	−9520	−6.400	0.000
0.300	−26571	−34209	−3.321	−14889	−8.400	0.000
0.400	−32238	−41448	−4.004	−19368	−9.600	0.000
0.500	−35480	−45225	−4.237	−22225	−10.000	0.000
0.600	−35790	−45000	−4.004	−22920	−9.600	0.000
0.700	−32787	−40425	−3.321	−21105	−8.400	0.000
0.800	−26193	−31344	−2.239	−16624	−6.400	0.000
0.900	−15730	−17793	−0.897	−9513	−3.600	0.000
1.000	0	0	0.000	0	0.000	0.000

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

Table IIIb. Partial quantities for Si in the liquid phase at 2300 K.

x_{Si}	ΔG_{Si} [J/mol]	ΔH_{Si} [J/mol]	ΔS_{Si} [J/(mol·K)]	$G_{\mathrm{Si}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Si}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Si}	γ_{Si}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−1238	−143	0.476	777	−0.400	0.937	1.041
0.800	−2743	−2156	0.255	1524	−1.600	0.866	1.083
0.700	−6524	−7983	−0.634	297	−3.600	0.711	1.016
0.600	−14041	−18992	−2.153	−4272	−6.400	0.480	0.800
0.500	−26230	−35975	−4.237	−12975	−10.000	0.254	0.507
0.400	−43551	−59148	−6.781	−26028	−14.400	0.103	0.256
0.300	−66095	−88151	−9.590	−43071	−19.600	0.032	0.105
0.200	−93946	−122048	−12.218	−63168	−25.600	0.007	0.037
0.100	−128840	−159327	−13.255	−84807	−32.400	0.001	0.012
0.000	$-\infty$	−197900	∞	−105900	−40.000	0.000	0.004

Reference state: Si(liquid)

Table IIIc. Partial quantities for V in the liquid phase at 2300 K.

x_{V}	ΔG_{V} [J/mol]	ΔH_{V} [J/mol]	ΔS_{V} [J/(mol·K)]	$G_{\mathrm{V}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{V}}^{\mathrm{E}}$ [J/(mol·K)]	a_{V}	γ_{V}
0.000	$-\infty$	−123900	∞	−31900	−40.000	0.000	0.189
0.100	−92876	−123363	−13.255	−48843	−32.400	0.008	0.078
0.200	−84474	−112576	−12.218	−53696	−25.600	0.012	0.060
0.300	−73347	−95403	−9.590	−50323	−19.600	0.022	0.072
0.400	−59535	−75132	−6.781	−42012	−14.400	0.044	0.111
0.500	−44730	−54475	−4.237	−31475	−10.000	0.096	0.193
0.600	−30617	−35568	−2.153	−20848	−6.400	0.202	0.336
0.700	−18512	−19971	−0.634	−11691	−3.600	0.380	0.543
0.800	−9255	−8668	0.255	−4988	−1.600	0.616	0.770
0.900	−3162	−2067	0.476	−1147	−0.400	0.848	0.942
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: V(liquid)

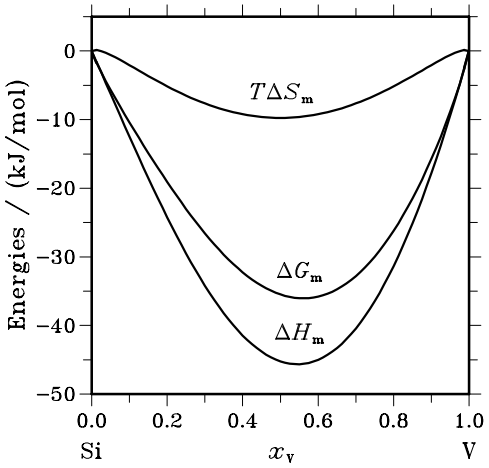

Fig. 2. Integral quantities of the liquid phase at T=2300 K.

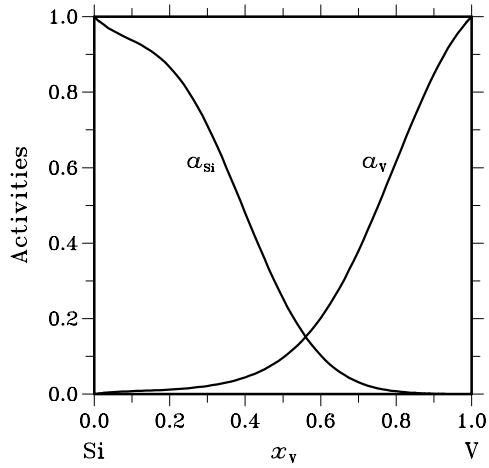

Fig. 3. Activities in the liquid phase at T=2300 K.

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

Compound	x_{V}	$\Delta_{\mathrm{f}}G^{\circ}$ / (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))
V_1Si_2	0.333	−39206	−40022	−2.736	0.165
V_6Si_5	0.545	−48298	−49216	−3.080	−0.865
V_5Si_3	0.625	−52410	−53643	−4.136	−0.508
V_3Si	0.750	−45583	−46572	−3.319	−1.425

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