Si – U (Silicon – Uranium)

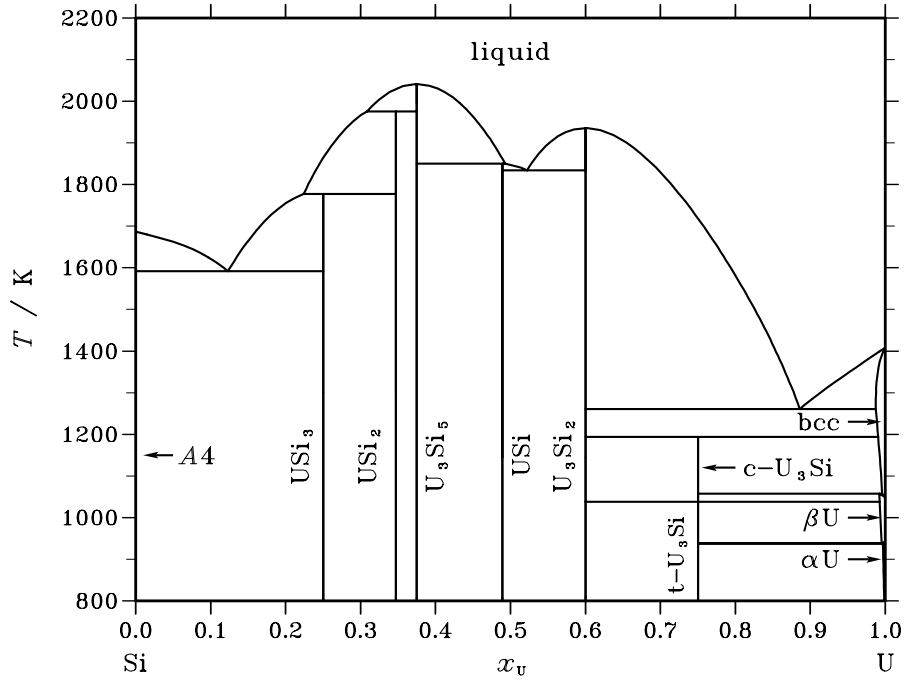

Fig. 1. Calculated phase diagram for the system Si-U.

The silicides of the Si-U binary system are interesting materials for the future in the nuclear field. A thermodynamic assessment of the system has been done by [04Che]. It is based on investigations of the phase diagram by Kaufman *et al.* [51Kau], Vaugeoyeau *et al.* [71Vau] (liquidus), Straatmann and Neumann [64Str], Khakimova *et al.* [63Kha] (solidus, solvus, U-rich domain). The elements are miscible in the liquid state. There is no reported solubility of uranium in crystalline Si, while the maximal solubility of silicon in the uranium solid solutions is 1.7 at.% at 1258 K [63Kha] for bcc, 1.134 at.% at 1068 K [64Str] or 1 at.% at 1058 K [63Kha] for βU, and 0.14 at.% at 938 K for αU. The following stoichiometric compounds have been selected: USi_3, $USi_{1.88}$, U_3Si_5, $U_{0.489}Si_{0.511}$, U_3Si_2, U_3Si (high/low temperature). U_3Si_5 and U_3Si_2 melt congruently at 2043 K and 1938 K, respectively [58Han, 71Vau].

The only available thermodynamic properties concern the stoichiometric compounds. The free energies, heats and entropies of formation of USi_3, USi_2, U_3Si_5, USi, U_3Si_2 have been determined by Alcock *et al.* [61Alc] (Knudsen vapour-pressure, solid/liquid equilibria, calorimetry). The heats of formation of USi_3, USi_2, USi, U_3Si_2 were determined calorimetrically by Gross *et al.* [61Gro]. The heat capacity of U_3Si, has been measured from 1 to 350 K and its enthalpy determined from 298 to 1160 K by Flotow *et al.* [77Flo]. $C_p(T)$, S(298.15K) and ΔH(t-U_3Si/c-U_3Si) at 1038 K are given. $\Delta_f H^\circ$ was reported from O'Hare *et al.* [75Oha]. The fundamental thermodynamic data are also reported by Barin [89Bar] for USi_3, USi_2, U_3Si_5, USi, U_3Si_2 and U_3Si.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Si,U)_1$
$A4$	$A4$	C(diamond)	$cF8$	$Fd\overline{3}m$	DIAMOND_A4	Si_1
USi_3	$L1_2$	$AuCu_3$	$cP4$	$Pm\overline{3}m$	USI3	U_1Si_3
USi_2	C_c	$ThSi_2$	$tI12$	$I4_1/amd$	USI2	$U_{25}Si_{47}$
U_3Si_5	$C32$	AlB_2	$hP3$	$P6/mmm$	U3SI5	U_3Si_5
USi	$B27$	FeB	$oP8$	$Pnma$	USI	$U_{511}Si_{489}$
U_3Si_2	$D5_a$	U_3Si_2	$tP10$	$P4/mbm$	U3SI2	U_3Si_2
c-U_3Si	$L1_2$	$AuCu_3$	$cP4$	$Pm\overline{3}m$	U3SI_H	U_3Si_1
t-U_3Si	···	···	$tI16$	$I4/mcm$	U3SI_L	U_3Si_1
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Si,U)_1$
βU	A_b	βU	$tP30$	$P4_2/mnm$	TETRAGONAL	$(Si,U)_1$
αU	$A20$	αU	$oC4$	$Cmcm$	ORTHORHOMBIC_A20	$(Si,U(_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_U			$\Delta_r H$ / (J/mol)
liquid ⇌ U_3Si_5	congruent	2041.2	0.375	0.375		−25778
liquid + U_3Si_5 ⇌ USi_2	peritectic	1975.4	0.308	0.375	0.347	−13141
liquid ⇌ U_3Si_2	congruent	1935.2	0.600	0.600		−16458
U_3Si_5 + liquid ⇌ USi	peritectic	1849.6	0.375	0.493	0.489	−18267
liquid ⇌ USi + U_3Si_2	eutectic	1833.5	0.522	0.489	0.600	−17406
liquid + USi_2 ⇌ USi_3	peritectic	1777.1	0.224	0.347	0.250	−22989
liquid ⇌ $A4$ + USi_3	eutectic	1591.9	0.123	0.000	0.250	−34814
liquid ⇌ U_3Si_2 + bcc	eutectic	1260.6	0.886	0.600	0.987	−6391
U_3Si_2 + bcc ⇌ c-U_3Si	peritectoid	1194.1	0.600	0.990	0.750	−1561
c-U_3Si + bcc ⇌ βU	peritectoid	1057.5	0.750	0.996	0.992	−4528
c-U_3Si ⇌ t-U_3Si	polymorphic	1038.0	0.750	0.750		−1077
βU ⇌ t-U_3Si + αU	eutectoid	937.9	0.995	0.750	0.997	−2838

Table IIIa. Integral quantities for the liquid phase at 2100 K.

x_U	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	−13002	−23218	−4.865	−7326	−7.568	0.000
0.200	−22765	−41203	−8.780	−14028	−12.941	0.000
0.300	−29321	−52910	−11.233	−18655	−16.312	0.000
0.400	−32346	−58129	−12.277	−20595	−17.873	0.000
0.500	−31984	−57297	−12.054	−19882	−17.817	0.000
0.600	−28768	−51321	−10.739	−17017	−16.335	0.000
0.700	−23449	−41386	−8.541	−12783	−13.620	0.000
0.800	−16793	−28771	−5.704	−8055	−9.865	0.000
0.900	−9299	−14670	−2.558	−3623	−5.261	0.000
1.000	0	0	0.000	0	0.000	0.000

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

Table IIIb. Partial quantities for Si in the liquid phase at 2100 K.

x_{Si}	ΔG_{Si} [J/mol]	ΔH_{Si} [J/mol]	ΔS_{Si} [J/(mol·K)]	G^E_{Si} [J/mol]	S^E_{Si} [J/(mol·K)]	a_{Si}	γ_{Si}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−1832	−2363	−0.253	8	−1.129	0.900	1.000
0.800	−6263	−11314	−2.405	−2367	−4.261	0.699	0.873
0.700	−14906	−27598	−6.044	−8678	−9.009	0.426	0.608
0.600	−27265	−49828	−10.744	−18346	−14.991	0.210	0.350
0.500	−41494	−75217	−16.059	−29391	−21.822	0.093	0.186
0.400	−55180	−100326	−21.498	−39181	−29.117	0.042	0.106
0.300	−66186	−121795	−26.481	−45164	−36.491	0.023	0.075
0.200	−73712	−137088	−30.179	−45611	−43.561	0.015	0.073
0.100	−80558	−145230	−30.796	−40354	−49.941	0.010	0.099
0.000	−∞	−147546	∞	−31528	−55.247	0.000	0.164

Reference state: Si(liquid)

Table IIIc. Partial quantities for U in the liquid phase at 2100 K.

x_U	ΔG_U [J/mol]	ΔH_U [J/mol]	ΔS_U [J/(mol·K)]	G^E_U [J/mol]	S^E_U [J/(mol·K)]	a_U	γ_U
0.000	−∞	−252400	∞	−69095	−87.288	0.000	0.019
0.100	−113538	−210911	−46.368	−73334	−65.513	0.001	0.015
0.200	−88773	−160761	−34.280	−60672	−47.662	0.006	0.031
0.300	−62957	−111972	−23.341	−41935	−33.351	0.027	0.091
0.400	−39967	−70580	−14.577	−23969	−22.196	0.101	0.253
0.500	−22475	−39377	−8.049	−10372	−13.812	0.276	0.552
0.600	−11161	−18651	−3.567	−2241	−7.814	0.528	0.880
0.700	−5133	−6924	−0.853	1095	−3.819	0.745	1.065
0.800	−2563	−1692	0.414	1334	−1.441	0.863	1.079
0.900	−1382	−164	0.580	458	−0.296	0.924	1.027
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: U(liquid)

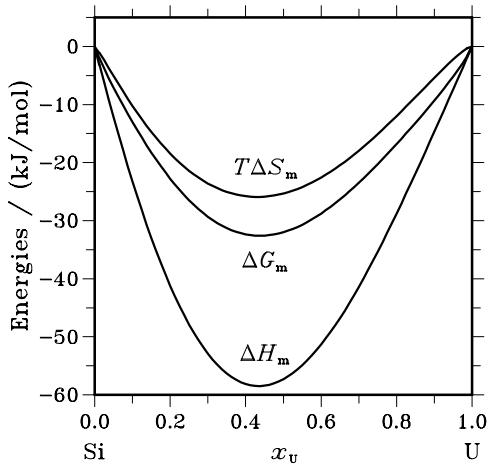

Fig. 2. Integral quantities of the liquid phase at T=2100 K.

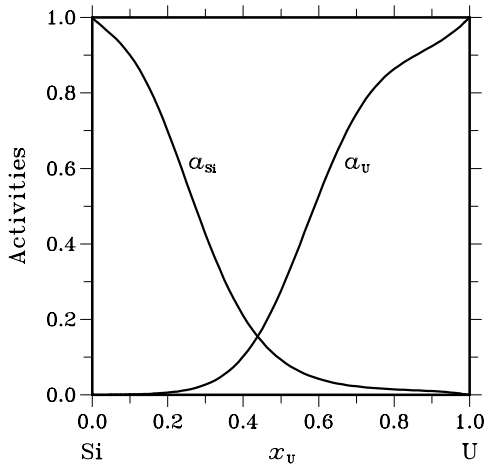

Fig. 3. Activities in the liquid phase at T=2100 K.

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

Compound	x_{U}	$\Delta_{\mathrm{f}}G^{\circ}$ / (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))
U_1Si_3	0.250	−33033	−33054	−0.070	1.046
USi_2	0.347	−43023	−43278	−0.856	1.058
U_3Si_5	0.375	−43306	−43428	−0.409	1.209
USi	0.489	−40836	−40867	−0.103	1.456
U_3Si_2	0.600	−35123	−34522	2.014	1.503
t-U_3Si_1	0.750	−21965	−21310	2.196	1.226

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