Mo – Si (Molybdenum – Silicon)

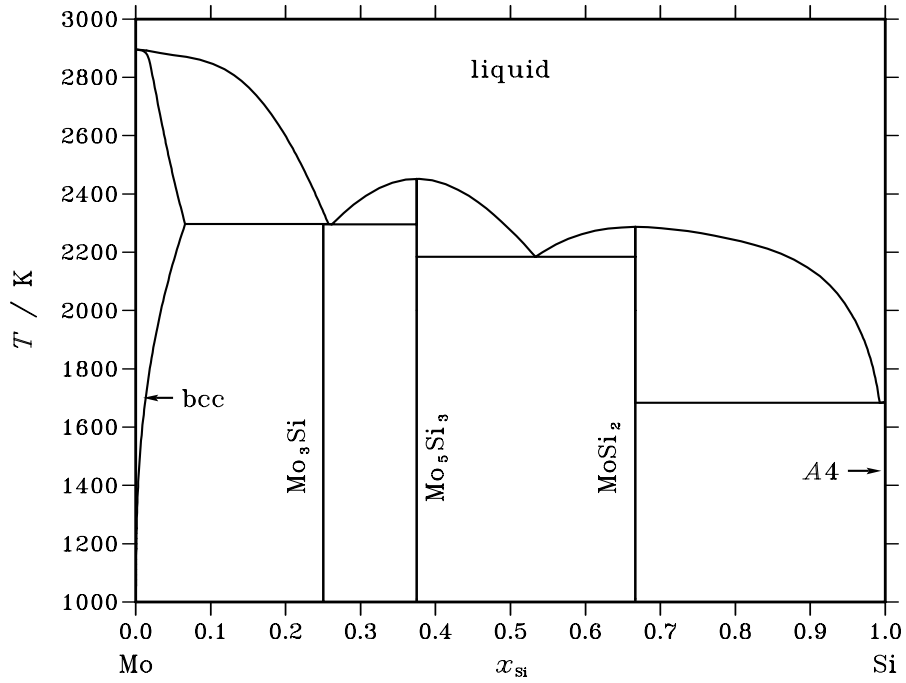

Fig. 1. Calculated phase diagram for the system Mo-Si.

The Mo-Si system has been assessed by [89Vah] and it was later revised by [03Che]. The phase diagram presents complete mutual solubility in the liquid state, a negligible solubility of Mo in pure Si, and a limited solubility of Si in bcc-Mo. There are three compounds in the system, Mo_3Si, Mo_5Si_3 and $MoSi_2$, presenting a narrow homogeneity range and two allotropic forms.
In Elliott [65Ell], the compound previously identified as Mo_3Si_2 was shown to be really Mo_5Si_3 [55Aro, 56Dau], isotypic with tetragonal Cr_5Si_3. Amberg [60Amb] determined the Mo-rich limit of $MoSi_2$. The thermodynamic properties of the intermetallic compounds have been determined in various experimental investigations which are reviewed in [89Vah].
The calculated phase diagram is in good agreement with the selected one of Brewer and Lamoreaux [80Bre]. The calculated enthalpy of mixing in the liquid is in agreement with calorimetric data [85Arp, 85Sud]. Further experimental work would be necessary to assess definitively the liquid enthalpy of mixing in the silicon rich domain, and the variation of activity with temperature, which is important for extrapolation of data at high temperatures.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Mo,Si)_1$
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Mo,Si)_1$
Mo_3Si	$A15$	Cr_3Si	$cP8$	$Pm\overline{3}n$	MO3SI	Mo_3Si_1
Mo_5Si_3	$D8_m$	W_5Si_3	$tI32$	$I4/mcm$	MO5SI3	Mo_5Si_3
$\beta MoSi_2$	$C40$	$CrSi_2$	$hP9$	$P6_222$	MOSI2	Mo_1Si_2
$\alpha MoSi_2$	$C11_b$	$MoSi_2$	$tI6$	$I4/mmm$	MOSI2	Mo_1Si_2
$A4$	$A4$	C(diamond)	$cF8$	$Fd\overline{3}m$	DIAMOND_A4	Si_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Si}			$\Delta_{\mathrm{r}}H$ / (J/mol)
liquid $\rightleftharpoons$ Mo_5Si_3	congruent	2452.0	0.375	0.375		−48601
bcc + liquid $\rightleftharpoons$ Mo_3Si	peritectic	2296.3	0.066	0.257	0.250	−46422
liquid $\rightleftharpoons$ Mo_3Si + Mo_5Si_3	eutectic	2295.5	0.261	0.250	0.375	−47507
liquid $\rightleftharpoons$ $MoSi_2$	congruent	2286.7	0.667	0.667		−62777
liquid $\rightleftharpoons$ Mo_5Si_3 + $MoSi_2$	eutectic	2184.6	0.533	0.375	0.667	−53323
liquid $\rightleftharpoons$ $MoSi_2$ + $A4$	eutectic	1683.3	0.993	0.667	1.000	−50431

Table IIIa. Integral quantities for the liquid phase at 3073 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	−16386	−10405	1.946	−8080	−0.756	0.000
0.200	−30289	−21636	2.816	−17503	−1.345	0.000
0.300	−40409	−30226	3.314	−24802	−1.765	0.000
0.400	−45569	−34572	3.578	−28373	−2.017	0.000
0.500	−45729	−34476	3.662	−28018	−2.101	0.000
0.600	−41672	−30675	3.578	−24476	−2.017	0.000
0.700	−34566	−24382	3.314	−18958	−1.765	0.000
0.800	−25468	−16816	2.816	−12683	−1.345	0.000
0.900	−14722	−8741	1.946	−6416	−0.756	0.000
1.000	0	0	0.000	0	0.000	0.000

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

Table IIIb. Partial quantities for Mo in the liquid phase at 3073 K.

x_{Mo}	ΔG_{Mo} [J/mol]	ΔH_{Mo} [J/mol]	ΔS_{Mo} [J/(mol·K)]	$G_{\mathrm{Mo}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Mo}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Mo}	γ_{Mo}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−1263	1170	0.792	1429	−0.084	0.952	1.058
0.800	−5669	−1001	1.519	33	−0.336	0.801	1.001
0.700	−17206	−10418	2.209	−8093	−0.756	0.510	0.729
0.600	−35233	−26314	2.902	−22181	−1.345	0.252	0.420
0.500	−56361	−45108	3.662	−38651	−2.101	0.110	0.220
0.400	−76379	−62266	4.593	−52967	−3.026	0.050	0.126
0.300	−92262	−74156	5.892	−61500	−4.119	0.027	0.090
0.200	−104500	−79909	8.002	−63378	−5.379	0.017	0.084
0.100	−121186	−83276	12.337	−62354	−6.808	0.009	0.087
0.000	$-\infty$	−94486	∞	−68657	−8.405	0.000	0.068

Reference state: Mo(liquid)

Table IIIc. Partial quantities for Si in the liquid phase at 3073 K.

x_{Si}	ΔG_{Si} [J/mol]	ΔH_{Si} [J/mol]	ΔS_{Si} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Si}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Si}}$ [J/(mol·K)]	a_{Si}	γ_{Si}
0.000	$-\infty$	−82752	∞	−56922	−8.405	0.000	0.108
0.100	−152489	−114578	12.337	−93656	−6.808	0.003	0.026
0.200	−128768	−104177	8.002	−87646	−5.379	0.006	0.032
0.300	−94550	−76445	5.892	−63788	−4.119	0.025	0.082
0.400	−61073	−46960	4.593	−37661	−3.026	0.092	0.229
0.500	−35097	−23844	3.662	−17386	−2.101	0.253	0.506
0.600	−18534	−9615	2.902	−5482	−1.345	0.484	0.807
0.700	−9838	−3050	2.209	−725	−0.756	0.680	0.972
0.800	−5710	−1042	1.519	−9	−0.336	0.800	1.000
0.900	−2893	−459	0.792	−201	−0.084	0.893	0.992
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Si(liquid)

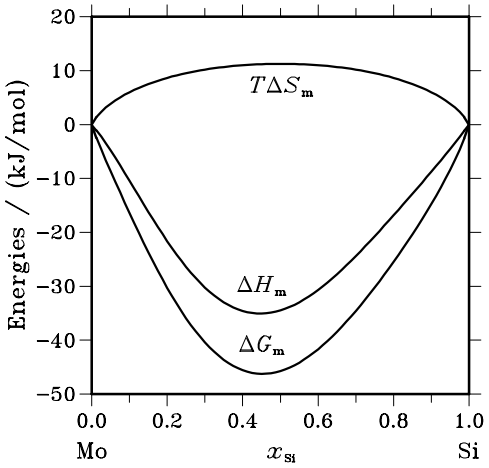

Fig. 2. Integral quantities of the liquid phase at T=3073 K.

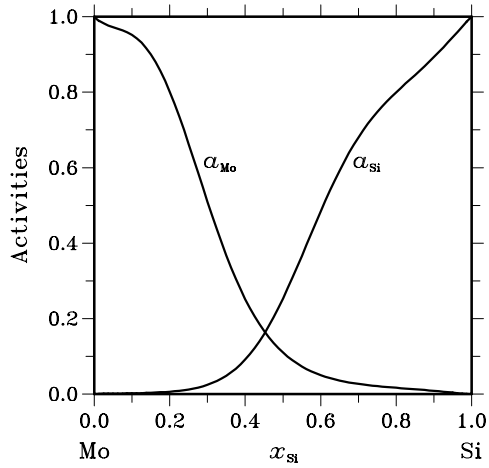

Fig. 3. Activities in the liquid phase at T=3073 K.

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))	$\Delta_{\mathrm{f}}C^{\circ}_{P}$ / (J/(mol·K))
Mo_3Si_1	0.250	−31222	−31066	0.522	−0.307
Mo_5Si_3	0.375	−40273	−39293	3.287	−0.249
Mo_1Si_2	0.667	−43633	−43689	−0.188	−0.056

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