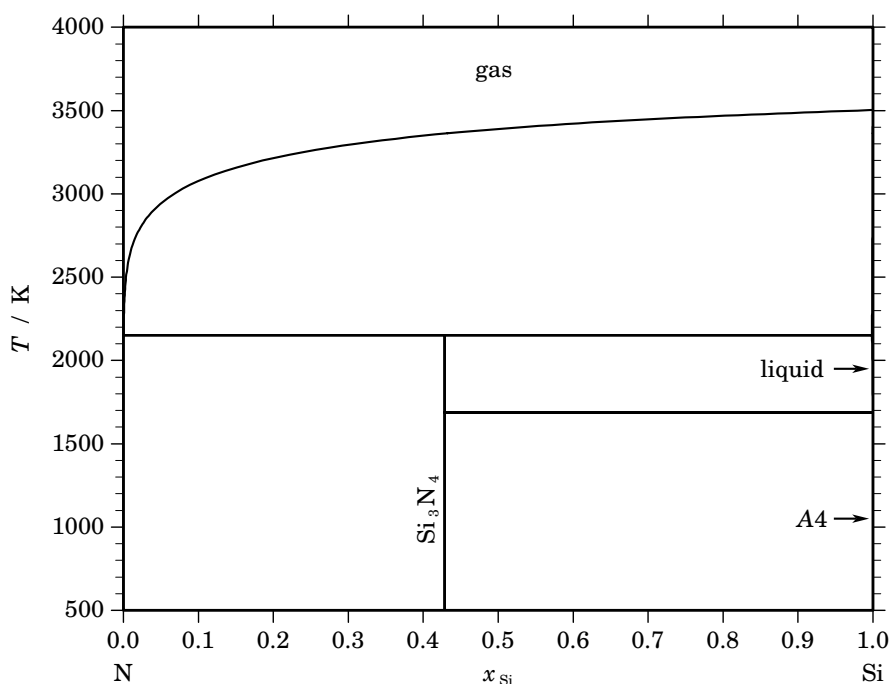


N – Si (Nitrogen – Silicon)**Fig. 1.** Calculated phase diagram for the system N-Si.

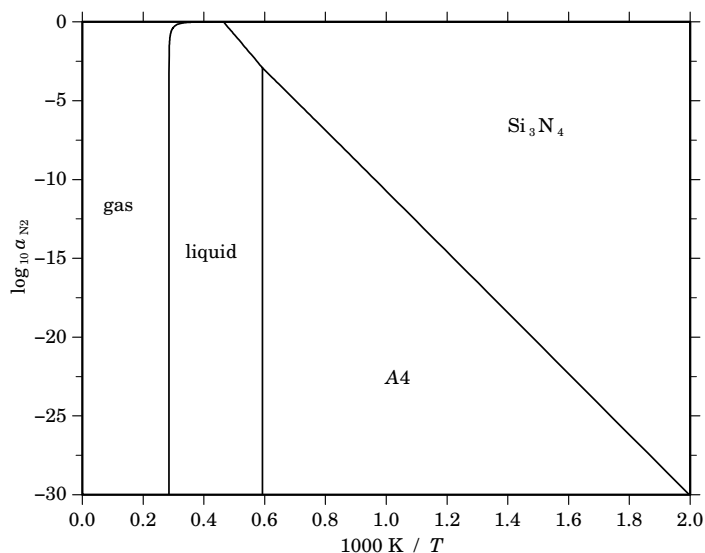
Silicon nitride, Si_3N_4 is a lightweight, strong and tough ceramic material which is of broad technical interest, e.g., for structural and wear-resistant applications up to high temperatures. A survey of the literature and a thermodynamic optimisation of the binary Si-N system has been given by [2003Ma]. The phase diagram of the Si-N system consists of a few phases only: solid Si (A4), the liquid, silicon nitride (Si_3N_4), and the gas phase. In the assessment [2003Ma] the solid phases have been treated as pure Si and Si_3N_4 , respectively. The very small solubility of nitrogen in solid Si which is known experimentally [1959Kai, 1973Yat] has been omitted from the assessment. The liquid has been modelled as a substitutional solution with the species Si and N and the gas phase has been modelled with the species N, N_2 , N_3 , SiN, Si_2N , Si, Si_2 , and Si_3 which have been taken from the SGTE substance database. The description for Si_3N_4 has been optimised based on the heat capacity values of [1976Guz] and on enthalpies of formation and entropies of formation mainly from [1959Peh]. Data for the eutectic have been selected from [1973Yat] and data for the decomposition of Si_3N_4 into liquid and gas are from [1981Dör]. Calculated partial pressures of nitrogen in the equilibrium of Si_3N_4 with Si-rich melt are in good agreement with the experimental data of [1930Hin].

Table I. Phases, structures and models.

Phase	Strukturbericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(\text{N},\text{Si})_1$
Si_3N_4	$hP14$	$P6_3$	SI3N4	Si_3N_4
A4	A4	C(diamond)	$cF8$	$Fd\bar{3}m$	DIAMOND_A4	Si_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Si}			$\Delta_r H / (\text{J/mol})$
gas + liquid $\rightleftharpoons \text{Si}_3\text{N}_4$	gas-peritectic	2152.0	0.000	0.999	0.429	–123303
liquid $\rightleftharpoons \text{Si}_3\text{N}_4 + \text{A4}$	eutectic	1686.9	1.000	0.429	1.000	–50217

**Fig. 2.** Calculated temperature-activity phase diagram. Reference state: $\frac{1}{2}\text{N}_2(\text{gas}, 0.1 \text{ MPa})$.**Table III.** Standard reaction quantities at 298.15 K for the compounds per mole of atoms.

Compound	x_{Si}	$\Delta_f G^\circ / (\text{J/mol})$	$\Delta_f H^\circ / (\text{J/mol})$	$\Delta_f S^\circ / (\text{J/(mol}\cdot\text{K)})$	$\Delta_f C_P^\circ / (\text{J/(mol}\cdot\text{K)})$
Si_3N_4	0.429	–91714	–105603	–46.583	–3.146

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