Li – N (Lithium – Nitrogen)

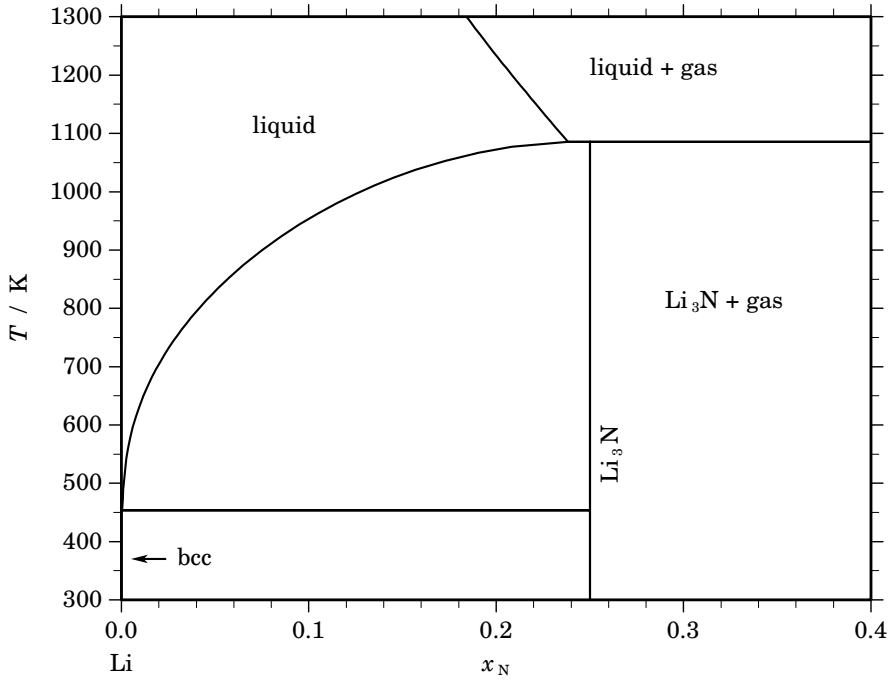

Fig. 1. Calculated phase diagram for the system Li-N.

Lithium nitride, LiN, can store more than 11% of its own weight in hydrogen which is considerably more than any other hydrogen storage material so far. Although there are still problems to solve for releasing the hydrogen from the storage the Li-N system will continue to be of high interest. The Li-N system has been reviewed by [1992San] and a thermodynamic optimisation has been reported in [2003Wan]. However the dataset of [2003Wan] leads to the formation of the liquid phase in the region where only LiN_3+gas should be stable and therefore, it has been re-assessed for the SGTE collection of binary systems [2005Fra]. The system Li-N includes 5 stable phases: gas, liquid, bcc-Li, Li_3N, and LiN_3. For the latter compound, lithium azide, no quantitative thermodynamic information seem to be available, except that under atmospheric pressure it does not melt but decomposes between 388 and 571 K. Therefore, it has not been included in the assessment. The solubility of nitrogen in solid lithium seems to be very small although no data have been reported. Therefore, bcc-Li has been treated as a pure substance. Similarly, Li_3N is described as a stoichiometric compound. The data for Li_3N are based on the SGTE substance database but with adjusted enthalpy and entropy. The solubility of nitrogen in molten Li has been measured in several investigations. A survey of these results is given in [2001Bor]. For the present optimisation a set of 3 investigations with the best agreement among them has been selected [1959Bol, 1975Ada, 1975Yon]. Since at lower temperatures the data of [1959Bol] deviate a bit too much from the other two sets the results of [1959Bol] have been used only for optimising the liquidus line above 800 K.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Li,N)_1$
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	Li_1
Li_3N	$\cdots$	Li_3N	$hP4$	$P6/mmm$	LI3N	Li_3N_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_N			$\Delta_r H$ / (J/mol)
liquid + gas $\rightleftharpoons$ Li_3N	gas-peritectic	1081.8	0.220	1.000	0.250	−25528
liquid $\rightleftharpoons$ bcc + Li_3N	eutectic	453.3	0.000	0.000	0.250	−3013

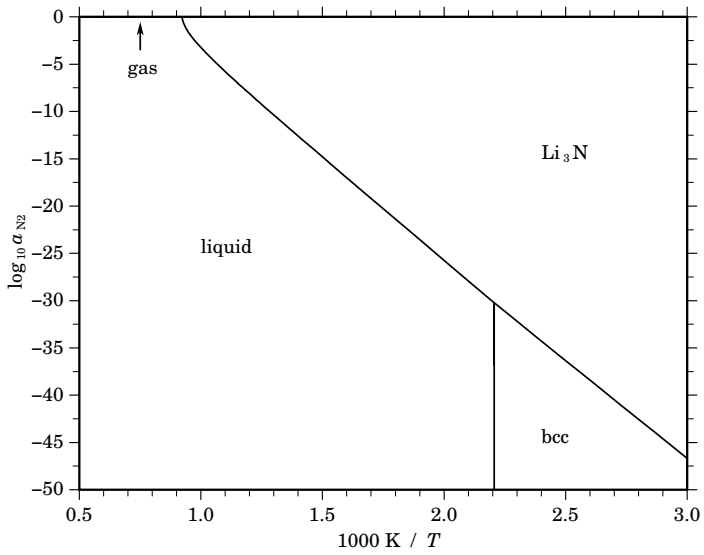

Fig. 2. Calculated temperature-activity phase diagram. Reference state: $\frac{1}{2}N_2$(gas, 0.1 MPa).

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

Compound	x_N	$\Delta_f G^\circ$ / (J/mol)	$\Delta_f H^\circ$ / (J/mol)	$\Delta_f S^\circ$ / (J/(mol·K))	$\Delta_f C_P^\circ$ / (J/(mol·K))
Li_3N_1	0.250	−32402	−41391	−30.149	−2.903

References

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