H – Nb (Hydrogen – Niobium)

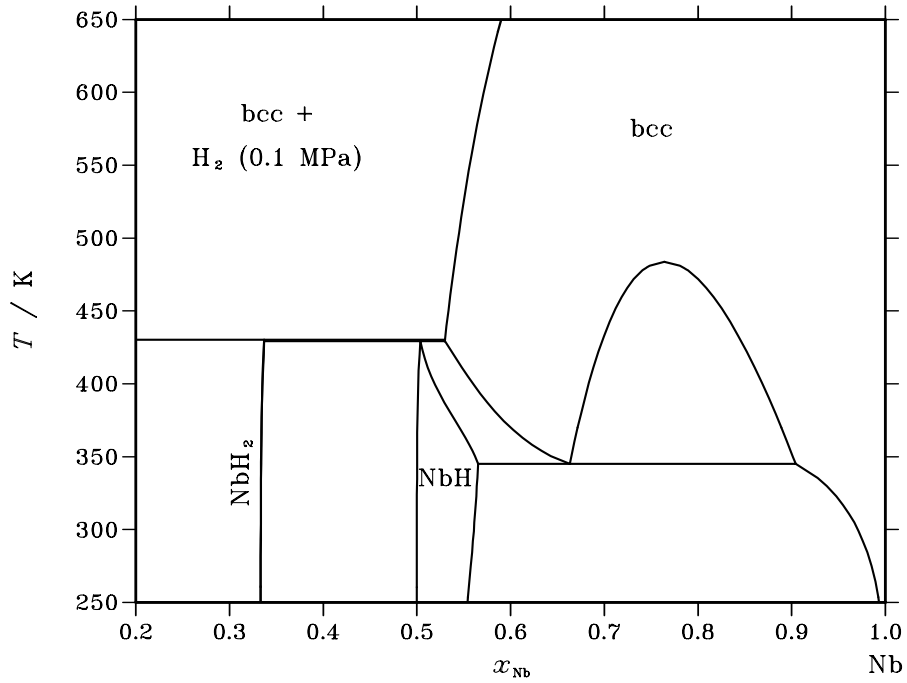

Fig. 1. Calculated phase diagram for the system H-Nb.

The thermodynamic assessment of the H-Nb system has been done by Ansara and Dupin [97Ans]. This system has been studied experimentally only at temperatures below 800 K and at low H content, i.e. for hydrogen pressures of about one atmosphere and below that. The phase diagram of this system is constituted by a miscibility gap in the bcc phase (Nb) and by a large number of hydrides phases. The reactions between these different phases are not very well known. Ansara and Dupin have only considered two of these hydrides: the βNbH phase, in equilibrium with the interstitial solution bcc and δNbH_2, isotypic with CaF_2. The assessment of the bcc phase takes into consideration only the data of P_{H_2} measured by Kuji and Oates [84Kuj] over a large pressure range with high purity Nb (99.99%) and the limit of the miscibility gap determined by X-ray diffraction [79Zab].
It has not been possible to get a perfect agreement with these two sets. When the critical temperature fits Zabel's results chosen by Smith in his critical assessment [83Smi], the highest hydrogen pressures measured by Oates and Kuji are not well reproduced by the calculation. The assessment is thus a compromise. The critical temperature is finally very close to the one determined by Pryde and Titcomb [69Pry], the limits of the miscibility gap in composition being shifted from the ones of this study towards higher H content, in better agreement with [79Zab] and [65Wal].

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$Nb_1(H,\Box)_3$
NbH	$\cdots$	$\cdots$	$oP8$	$\cdots$	NBH_BETA	$Nb_1(H,\Box)_1$
NbH_2	$C1$	CaF_2	$cF12$	$Fm\overline{3}m$	FCC_C1	$Nb_1(H,\Box)_2$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Nb}			$\Delta_{\mathrm{r}}H$ / (J/mol)
bcc $\rightleftharpoons$ bcc′ + bcc″	critical	483.6	0.764	0.764	0.764	0
gas + bcc′ $\rightleftharpoons$ NbH_2	gas-peritectoid	430.2	0.000	0.530	0.337	−7841
NbH_2 + bcc′ $\rightleftharpoons$ NbH	peritectoid	429.3	0.337	0.530	0.504	−8306
bcc′ $\rightleftharpoons$ NbH + bcc″	monotectoid	345.0	0.663	0.565	0.904	−4118

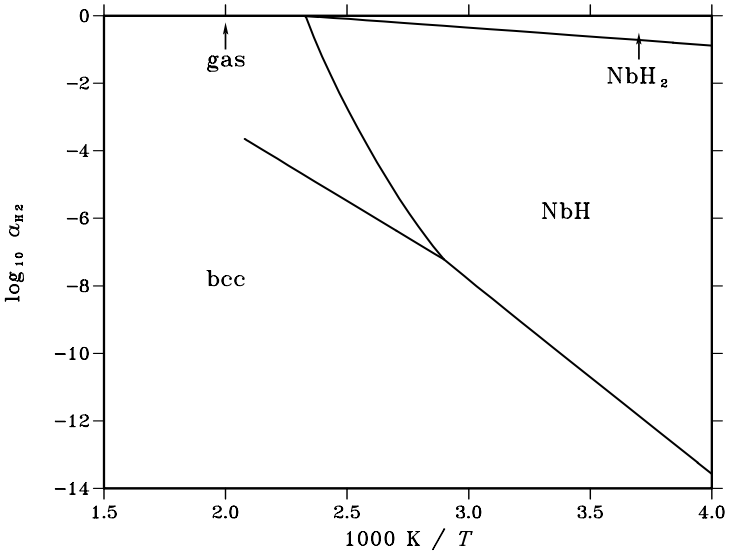

Fig. 2. Calculated temperature-activity phase diagram. Reference state: $\frac{1}{2}H_2$(gas, 0.1 MPa).

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

Compound	x_{Nb}	$\Delta_{\mathrm{f}}G^\circ$ / (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))
NbH_2	0.333	−9567	−19996	−34.979	0.162
NbH	0.500	−13577	−27454	−46.543	0.032

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