H – Zr (Hydrogen – Zirconium)

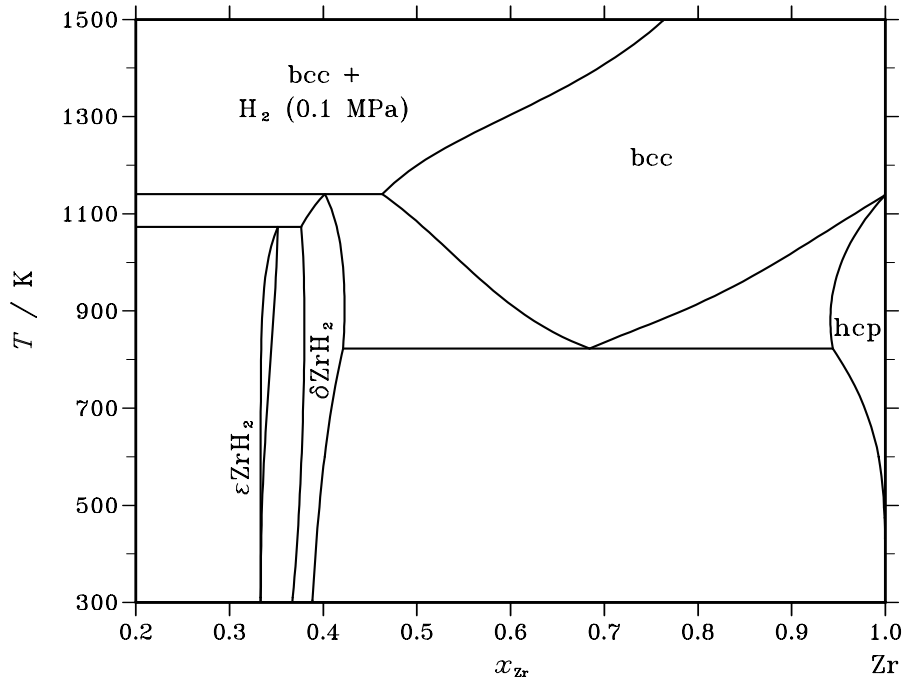

Fig. 1. Calculated phase diagram for the system H-Zr.

The H-Zr phase diagram was thermodynamically assessed by Dupin *et al.* [99Dup]. Their work is based on experimental data from the literature [55Gul, 59Lag, 60Lib, 60Som, 62Bec, 62Lib, 67Kea, 69Moo, 83Rit, 90Zuz]. No experimental data involving the liquid phase are available. In the temperature range up to 1500 K the system is of the eutectoid type and consists of the hcp-Zr phase (with interstitially dissolved H), bcc-Zr (with interstitially dissolved H) δZrH_2 phase and ϵZrH_2. The two hydrides were described with a 2-sublattice model, where the second sublattice is mainly occupied by hydrogen. The gas phase used in the assessment was described as an ideal mixture of H, H_2, Zr, Zr_2 and HZr. At low hydrogen levels, the phase fields are well known and the calculated solid-solid equilibria are in satisfactory agreement with the experimental results. The calculated solubilities of H in hcp-Zr are in fairly good agreement with available experimental data. Concerning the $\delta ZrH_2/\epsilon ZrH_2$ equilibrium, some discrepancies exist regarding the question whether a transformation of higher order might exist between these two phases. These may be traced to the experimental difficulties in obtaining genuine stable equilibrium, as well as to the effects of oxygen impurities, which tend to stabilise the $\delta ZrH_2/\epsilon ZrH_2$ two-phase field [63Sin]. [62Bec] identified a metastable hydride, γZr, which appeared on cooling into the lower temperature range of the hcp-Zr/δZrH_2 region. However, [72Mis] disagreed with this result and suggested that γZrH was a stable phase formed at about 528 K in a peritectoid reaction. Currently, the existence of the peritectoid reaction has been discarded on the basis of experimental results, and the generally accepted opinion [83Nor] is that γZrH is in fact a metastable phase.

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	$Zr_1(H,\Box)_3$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$Zr_1(H,\Box)_1$
δZrH_2	$C1$	CaF_2	$cF14$	$Fm\overline{3}m$	FCC_C1	$Zr_1(H,\Box)_2$
ϵZrH_2	L'_b	ThH_2	$tI6$	$I4/mmm$	ZRH2_EPSILON	$Zr_1(H,\Box)_2$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Zr}			$\Delta_r H$ / (J/mol)
gas + bcc $\rightleftharpoons$ δZrH_2	gas-peritectoid	1140.7	0.000	0.463	0.402	−19026
gas + δZrH_2 $\rightleftharpoons$ εZrH_2	gas-peritectoid	1173.1	0.000	0.377	0.351	−6239
bcc $\rightleftharpoons$ δZrH_2 + hcp	eutectoid	822.3	0.684	0.421	0.944	−8275

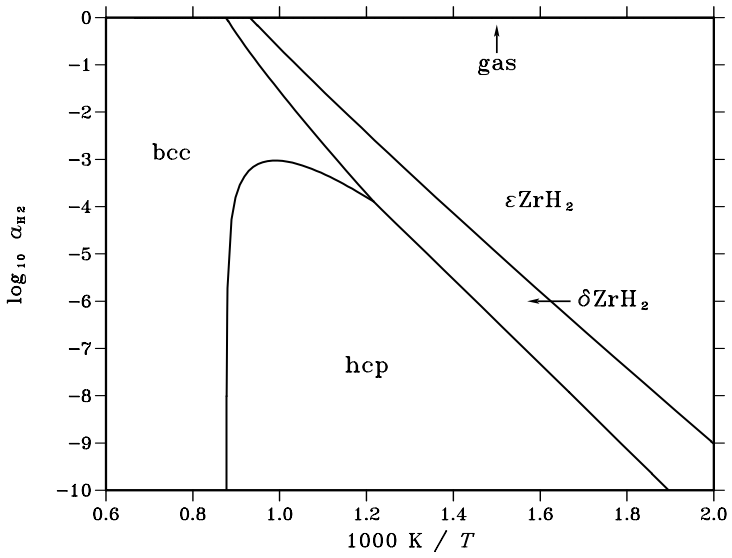

Fig. 2. Calculated temperature-activity phase diagram. Reference state: $\frac{1}{2}H_2$(gas, 0.1 MPa).

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

Compound	x_{Zr}	$\Delta_f G^\circ$ / (J/mol)	$\Delta_f H^\circ$ / (J/mol)	$\Delta_f S^\circ$ / (J/(mol·K))	$\Delta_f C_P^\circ$ / (J/(mol·K))
ϵZrH_2	0.333	−42900	−56454	−45.459	−1.206
δZrH_2	0.367	−41753	−55416	−45.825	2.997

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