U – Zr (Uranium – Zirconium)

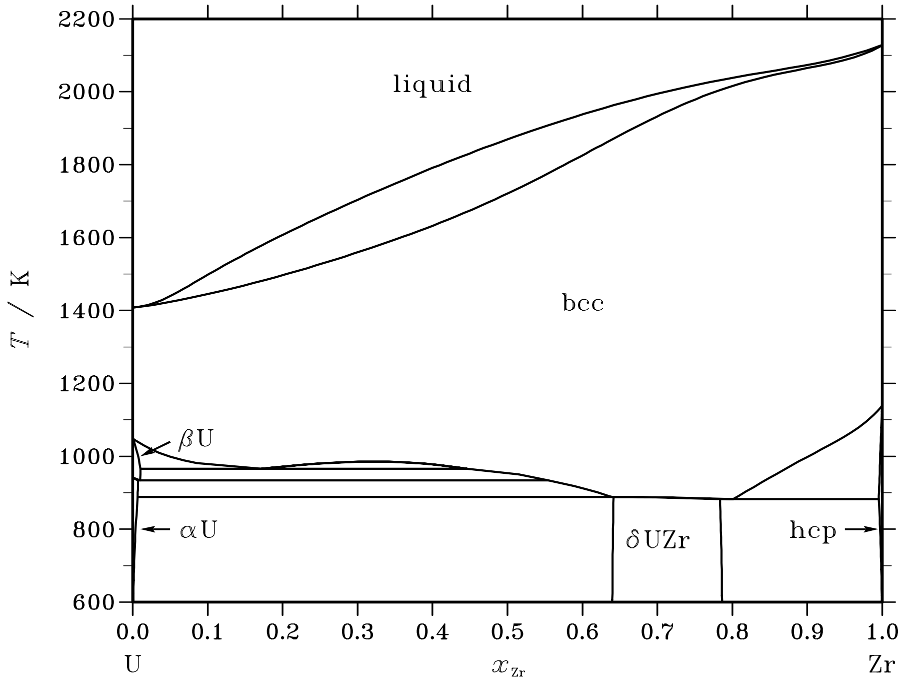

Fig. 1. Calculated phase diagram for the system U-Zr.

The U-Zr system is of first importance for nuclear safety applications. It was already assessed by Leibowitz *et al.* [89Lei] and Ogawa *et al.* [91Oga], but the thermodynamic properties of the solid solutions and liquid phases were not conciliable and extrapolable. That is the reason why it was entirely re-assessed by Chevalier *et al.* [04Che].

A simple one-lattice substitutional model was used for the solution phases liquid, bcc, hcp, αU, and βU, and a two-sublattice model for the non-stoichiometric intermetallic δUZr-phase. The phase diagram was presented in the compilations of Sheldon and Peterson [89She] and Okamoto [93Oka]. It presents complete solubility of uranium and zirconium in the liquid phase and bcc solid solution at high temperature. The bcc solid solution presents a miscibility gap below 993 K. The solubility of Zr in αU and βU and of U in hcp-Zr is limited. The intermetallic δUZr-phase exhibits a non-negligible stoichiometry range. It is based on experimental work of Summers-Smith [54Sum] on the solid and liquid states (metallography, dilatometry, X-ray), Philibert and Adda [57Phi] (chemical diffusion), Duffey and Bruch [58Duf] (metallography, cooling-rate studies), Zegler [62Zeg], Leibowitz *et al.* [89Lei], Ohmichi [89Ohm], Maeda *et al.* [92Mae], Akabori *et al.* [92Aka], Howlett and Knapton [58How]. The thermodynamic properties were experimentally determined by Nagarajan *et al.* [93Nag] (calorimetry), Kanno *et al.* [88Kan] (mass spectrometry, 1700 K - 2060 K), Maeda *et al.* [92Mae] (mass spectrometry).

The calculated phase diagram is in good agreement with the experimental results both in the solid and liquid states. The activity of uranium is in agreement with the experimental ones of Maeda *et al.* [92Mae]. However, further work should be made for evaluating the quality of the extrapolation of the excess Gibbs energy of the liquid phase at temperatures well above the liquidus, interesting the nuclear safety field.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(U,Zr)_1$
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(U,Zr)_1$
αU	$A20$	αU	$oC4$	$Cmcm$	ORTHORHOMBIC_A20	$(U,Zr)_1$
βU	A_b	βU	$tP30$	$P4_2/mnm$	TETRAGONAL	$(U,Zr)_1$
δUZr	$C32$	AlB_2	$hP3$	$P6/mmm$	DELTA	$(U,Zr)_2Zr_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(U,Zr)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Zr}			$\Delta_r H$ / (J/mol)
bcc ⇌ bcc′ + bcc″	critical	985.1	0.322	0.322	0.322	0
bcc′ ⇌ βU + bcc″	monotectoid	965.5	0.172	0.010	0.446	−5640
βU ⇌ αU + bcc″	eutectoid	934.2	0.010	0.007	0.554	−2795
bcc″ ⇌ δUZr	congruent	888.4	0.645	0.645		−14927
bcc″ ⇌ αU + δUZr	eutectoid	888.4	0.640	0.007	0.641	−15011
bcc″ ⇌ δUZr + hcp	eutectoid	882.9	0.801	0.783	0.995	−11798

Table IIIa. Integral quantities for the liquid phase at 2200 K.

x_{Zr}	ΔG_m [J/mol]	ΔH_m [J/mol]	ΔS_m [J/(mol·K)]	G_m^E [J/mol]	S_m^E [J/(mol·K)]	ΔC_P [J/(mol·K)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−7297	1944	4.200	−1351	1.497	−5.547
0.200	−11456	3554	6.823	−2303	2.662	−9.862
0.300	−14067	4793	8.573	−2894	3.494	−12.944
0.400	−15470	5625	9.589	−3160	3.993	−14.793
0.500	−15817	6013	9.922	−3138	4.159	−15.409
0.600	−15176	5919	9.589	−2865	3.993	−14.793
0.700	−13552	5308	8.573	−2378	3.494	−12.944
0.800	−10867	4142	6.823	−1714	2.662	−9.862
0.900	−6855	2385	4.200	−909	1.497	−5.547
1.000	0	0	0.000	0	0.000	0.000

Reference states: U(liquid), Zr(liquid)

Table IIIb. Partial quantities for U in the liquid phase at 2200 K.

x_U	ΔG_U [J/mol]	ΔH_U [J/mol]	ΔS_U [J/(mol·K)]	G_U^E [J/mol]	S_U^E [J/(mol·K)]	a_U	γ_U
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−2133	161	1.042	−205	0.166	0.890	0.989
0.800	−4854	692	2.521	−772	0.665	0.767	0.959
0.700	−8151	1668	4.463	−1627	1.497	0.640	0.915
0.600	−12039	3161	6.909	−2695	2.662	0.518	0.863
0.500	−16584	5246	9.922	−3905	4.159	0.404	0.808
0.400	−21942	7995	13.608	−5181	5.989	0.301	0.753
0.300	−28474	11484	18.163	−6451	8.152	0.211	0.703
0.200	−37080	15785	24.029	−7641	10.648	0.132	0.659
0.100	−50795	20971	32.621	−8676	13.476	0.062	0.622
0.000	$-\infty$	27117	∞	−9485	16.637	0.000	0.595

Reference state: U(liquid)

Table IIIc. Partial quantities for Zr in the liquid phase at 2200 K.

x_{Zr}	ΔG_{Zr} [J/mol]	ΔH_{Zr} [J/mol]	ΔS_{Zr} [J/(mol·K)]	G_{Zr}^E [J/mol]	S_{Zr}^E [J/(mol·K)]	a_{Zr}	γ_{Zr}
0.000	$-\infty$	20983	∞	−15619	16.637	0.000	0.426
0.100	−53777	17990	32.621	−11658	13.476	0.053	0.529
0.200	−37866	14999	24.029	−8426	10.648	0.126	0.631
0.300	−27873	12085	18.163	−5850	8.152	0.218	0.726
0.400	−20617	9321	13.608	−3856	5.989	0.324	0.810
0.500	−15050	6779	9.922	−2371	4.159	0.439	0.878
0.600	−10665	4535	6.909	−1321	2.662	0.558	0.930
0.700	−7157	2661	4.463	−633	1.497	0.676	0.966
0.800	−4314	1232	2.521	−232	0.665	0.790	0.987
0.900	−1973	320	1.042	−46	0.166	0.898	0.998
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Zr(liquid)

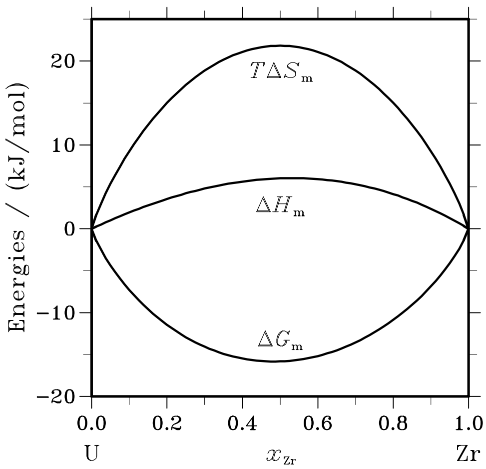

Fig. 2. Integral quantities of the liquid phase at T=2200 K.

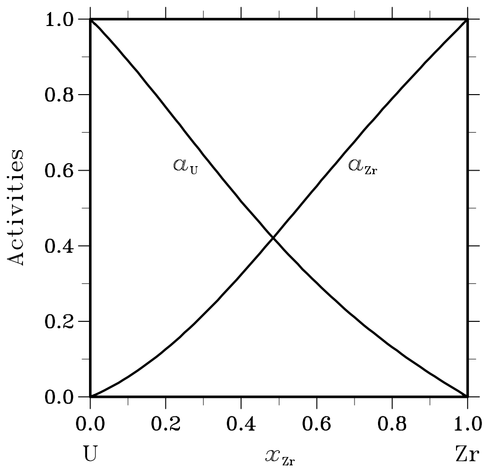

Fig. 3. Activities in the liquid phase at T=2200 K.

Table IVa. Integral quantities for the stable phases at 1273 K.

Phase	x_{Zr}	ΔG_{m} [J/mol]	ΔH_{m} [J/mol]	ΔS_{m} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{m}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{m}}$ [J/(mol·K)]	ΔC_P [J/(mol·K)]
bcc	0.000	0	0	0.000	0	0.000	0.000
	0.100	−2384	3294	4.460	1057	1.757	−2.230
	0.200	−3797	5476	7.285	1499	3.124	−3.965
	0.300	−4883	6803	9.179	1583	4.100	−5.204
	0.400	−5717	7371	10.282	1406	4.686	−5.947
	0.500	−6293	7258	10.645	1044	4.881	−6.195
	0.600	−6511	6577	10.282	612	4.686	−5.947
	0.700	−6198	5488	9.179	268	4.100	−5.204
	0.800	−5158	4116	7.285	139	3.124	−3.965
	0.900	−3255	2423	4.460	186	1.757	−2.230
	1.000	0	0	0.000	0	0.000	0.000

Reference states: U(bcc), Zr(bcc)

Table IVb. Partial quantities for U in the stable phases at 1273 K.

Phase	x_{U}	ΔG_{U} [J/mol]	ΔH_{U} [J/mol]	ΔS_{U} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{U}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{U}}$ [J/(mol·K)]	a_{U}	γ_{U}
bcc	1.000	0	0	0.000	0	0.000	1.000	1.000
	0.900	−743	620	1.071	372	0.195	0.932	1.036
	0.800	−1341	2016	2.636	1021	0.781	0.881	1.101
	0.700	−2019	3993	4.723	1756	1.757	0.826	1.180
	0.600	−2863	6521	7.371	2544	3.124	0.763	1.272
	0.500	−4188	9362	10.645	3148	4.881	0.673	1.346
	0.400	−6597	12050	14.648	3102	7.029	0.536	1.340
	0.300	−10727	14196	19.578	2016	9.568	0.363	1.210
	0.200	−16802	16141	25.878	233	12.496	0.204	1.022
	0.100	−24565	19940	34.961	−194	15.816	0.098	0.982
	0.000	$-\infty$	30685	∞	5829	19.526	0.000	1.734

Reference state: U(bcc)

Table IVc. Partial quantities for Zr in the stable phases at 1273 K.

Phase	x_{Zr}	ΔG_{Zr} [J/mol]	ΔH_{Zr} [J/mol]	ΔS_{Zr} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Zr}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Zr}}$ [J/(mol·K)]	a_{Zr}	γ_{Zr}
bcc	0.000	$-\infty$	40122	∞	15266	19.526	0.000	4.230
	0.100	−17150	27355	34.961	7222	15.816	0.198	1.978
	0.200	−13624	19319	25.878	3411	12.496	0.276	1.380
	0.300	−11565	13358	19.578	1178	9.568	0.335	1.118
	0.400	−9999	8647	14.648	−301	7.029	0.389	0.972
	0.500	−8398	5153	10.645	−1061	4.881	0.452	0.905
	0.600	−6455	2929	7.371	−1048	3.124	0.543	0.906
	0.700	−4257	1756	4.723	−481	1.757	0.669	0.956
	0.800	−2247	1109	2.636	115	0.781	0.809	1.011
	0.900	−887	476	1.071	228	0.195	0.920	1.022
	1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Zr(bcc)

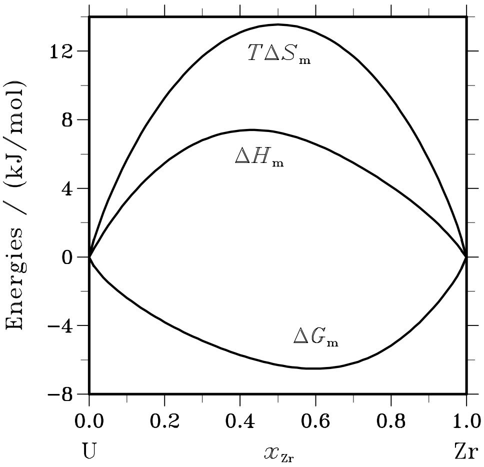

Fig. 4. Integral quantities of the stable phases at T=1273 K.

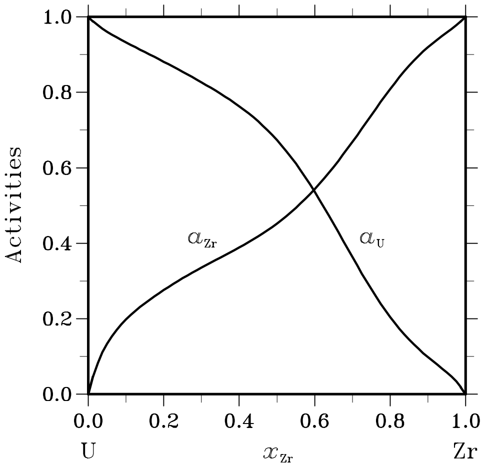

Fig. 5. Activities in the stable phases at T=1273 K.

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