Ge – Zn (Germanium – Zinc)

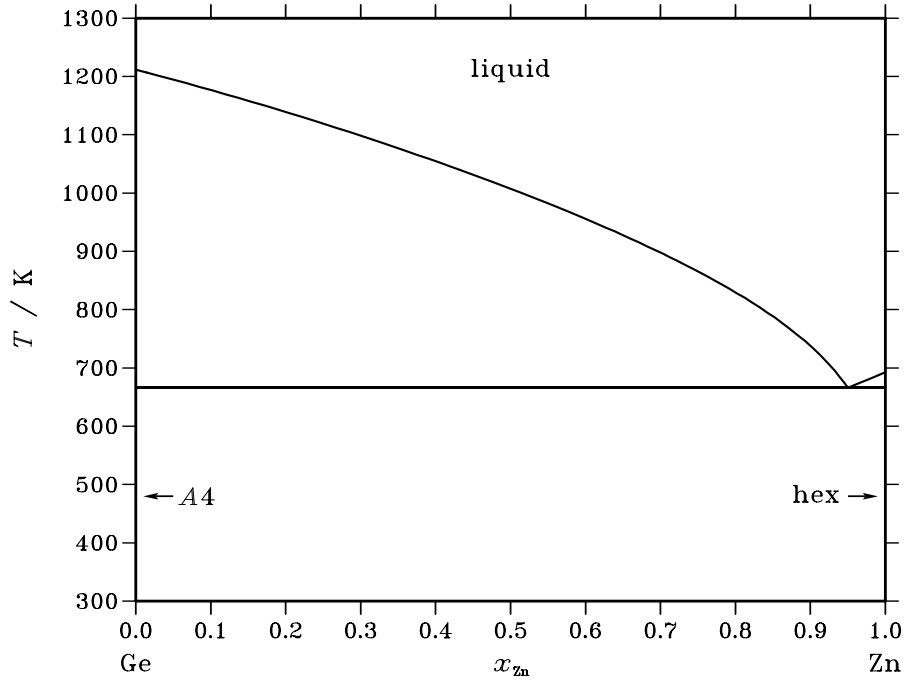

Fig. 1. Calculated phase diagram for the system Ge-Zn.

A thermodynamic assessment of the Ge-Zn system has been given by Chevalier [89Che] and it was later revised [03Che]. The phase diagram is rather simple and of eutectic type, located on the Zn rich side, with a complete mutual solubility in the liquid state, an unknown but negligible solubility of Ge in pure zinc, and a very small retrograde solid solubility of Zn in solid Ge [60Tru], which is $2.2 \cdot 10^{-4}$ at the eutectic. There is no compound in the system and the solution phases have been described with simple substitutional models. The liquidus has been determined by thermal and microscopic analysis [42Geb], by solubility measurements [60Thu] and with EMF methods [59Kle].
The partial free energy of Zn in liquid alloys has been obtained from vapour pressure measurements [59Vor], and from EMF experiments [72Pre]. The shape of the activity curves of [72Pre] is very strange and shows a discontinuity between the points x_{Zn} = 0.8, 0.9, which seem to be acceptable, and the points x_{Zn} = 0.55, 0.6, and 0.7, which were discarded. The deviation from ideality is strangely very negative for [59Vor] and these points have also been discarded. The thermodynamic properties of the liquid have been obtained from EMF measurements by Batalin *et al.* [70Bat]. They show a slight deviation from ideality and a positive enthalpy of mixing. Further experimental work would be necessary to assess directly the enthalpy of mixing of liquid alloys and the variation of activity with temperature, which is important for extrapolation of data at high temperatures.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Ge,Zn)_1$
$A4$	$A4$	C(diamond)	$cF8$	$Fd\overline{3}m$	DIAMOND_A4	$(Ge,Zn)_1$
hex	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	Zn_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Zn}			$\Delta_{\mathrm{r}}H$ / (J/mol)
liquid $\rightleftharpoons$ $A4$ + hex	eutectic	665.8	0.950	0.000	1.000	−8916

Table IIIa. Integral quantities for the liquid phase at 1273 K.

x_{Zn}	ΔG_{m} [J/mol]	ΔH_{m} [J/mol]	ΔS_{m} [J/(mol·K)]	$G_{\mathrm{m}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{m}}^{\mathrm{E}}$ [J/(mol·K)]	ΔC_P [J/(mol·K)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−3713	274	3.132	−272	0.429	0.000
0.200	−5780	488	4.924	−484	0.763	0.000
0.300	−7100	640	6.080	−635	1.001	0.000
0.400	−7849	731	6.740	−725	1.144	0.000
0.500	−8092	762	6.955	−756	1.192	0.000
0.600	−7849	731	6.740	−725	1.144	0.000
0.700	−7100	640	6.080	−635	1.001	0.000
0.800	−5780	488	4.924	−484	0.763	0.000
0.900	−3713	274	3.132	−272	0.429	0.000
1.000	0	0	0.000	0	0.000	0.000

Reference states: Ge(liquid), Zn(liquid)

Table IIIb. Partial quantities for Ge in the liquid phase at 1273 K.

x_{Ge}	ΔG_{Ge} [J/mol]	ΔH_{Ge} [J/mol]	ΔS_{Ge} [J/(mol·K)]	$G_{\mathrm{Ge}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Ge}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Ge}	γ_{Ge}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−1145	30	0.924	−30	0.048	0.897	0.997
0.800	−2483	122	2.046	−121	0.191	0.791	0.989
0.700	−4047	274	3.395	−272	0.429	0.682	0.975
0.600	−5890	488	5.010	−484	0.763	0.573	0.955
0.500	−8092	762	6.955	−756	1.192	0.466	0.931
0.400	−10787	1097	9.335	−1088	1.717	0.361	0.902
0.300	−14224	1493	12.347	−1481	2.337	0.261	0.869
0.200	−18969	1950	16.434	−1935	3.052	0.167	0.833
0.100	−26820	2469	23.007	−2448	3.862	0.079	0.793
0.000	$-\infty$	3048	∞	−3023	4.768	0.000	0.752

Reference state: Ge(liquid)

Table IIIc. Partial quantities for Zn in the liquid phase at 1273 K.

x_{Zn}	ΔG_{Zn} [J/mol]	ΔH_{Zn} [J/mol]	ΔS_{Zn} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Zn}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Zn}}$ [J/(mol·K)]	a_{Zn}	γ_{Zn}
0.000	$-\infty$	3048	∞	−3023	4.768	0.000	0.752
0.100	−26820	2469	23.007	−2448	3.862	0.079	0.793
0.200	−18969	1950	16.434	−1935	3.052	0.167	0.833
0.300	−14224	1493	12.347	−1481	2.337	0.261	0.869
0.400	−10787	1097	9.335	−1088	1.717	0.361	0.902
0.500	−8092	762	6.955	−756	1.192	0.466	0.931
0.600	−5890	488	5.010	−484	0.763	0.573	0.955
0.700	−4047	274	3.395	−272	0.429	0.682	0.975
0.800	−2483	122	2.046	−121	0.191	0.791	0.989
0.900	−1145	30	0.924	−30	0.048	0.897	0.997
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Zn(liquid)

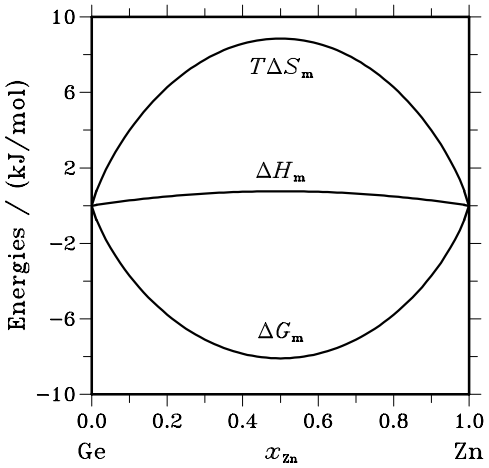

Fig. 2. Integral quantities of the liquid phase at T=1273 K.

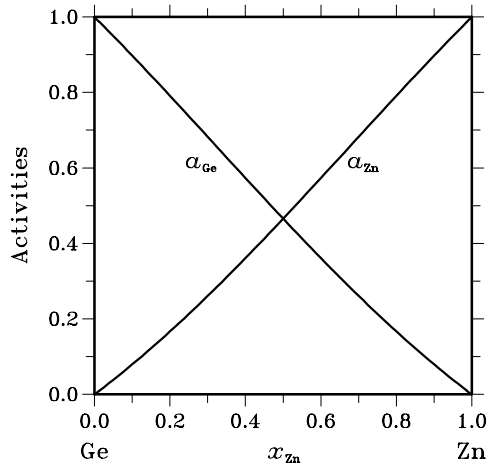

Fig. 3. Activities in the liquid phase at T=1273 K.

References

[42Geb] E. Gebhardt: Z. Metallkd. **34** (1942) 255–257.

[59Kle] O.J. Kleppa, C.E. Thalmayer: J. Phys. Chem. **63** (1959) 1953–1958.

[59Vor] G.F. Voronin, A.M. Evseev: Zh. Fiz. Khim. **33** (1959) 2024–2029.

[60Thu] C.D. Thurmond, M. Kowalchik: Bell System Tech. J. **39** (1960) 169–204.

[60Tru] F.A. Trumbore: Bell System Tech. J. **39** (1960) 205–233.

[70Bat] G.I. Batalin, E.A. Beloborodova, V.A. Stukalo: Izv. Akad. Nauk SSSR, Met. **2** (1970) 147–151.

[72Pre] B. Predel, U. Schallner: Z. Metallkd. **63** (1972) 119-125.

[89Che] P.-Y. Chevalier: Thermochim. Acta **155** (1989) 227–240.

[03Che] P.-Y. Chevalier, E. Fischer: unpublished work, 2003.