Ag – Ca (Silver – Calcium)

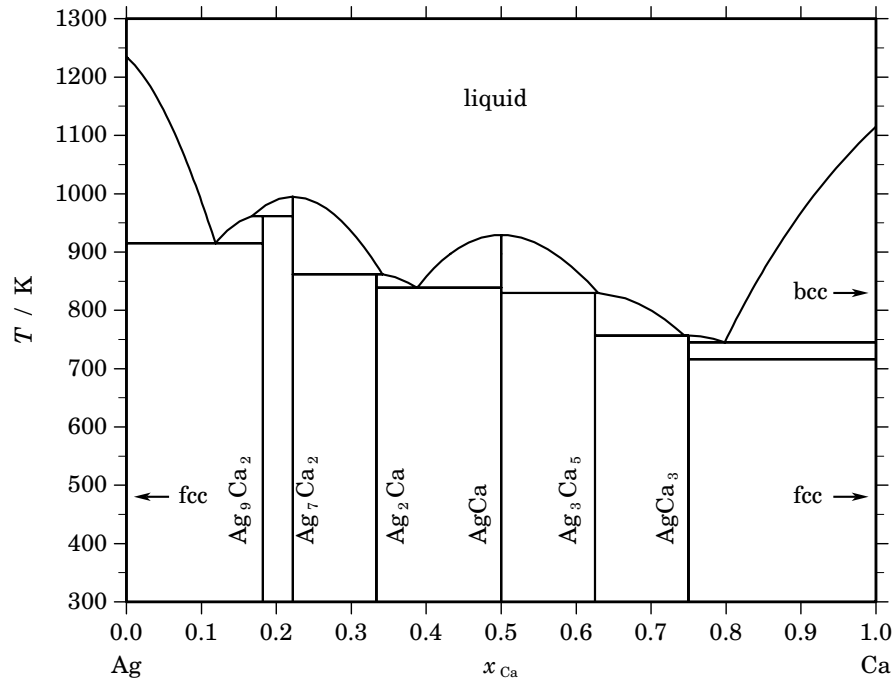

Fig. 1. Calculated phase diagram for the system Ag-Ca.

The Ag-Ca binary system contains two components interesting the nuclear field, silver being part of AIC control rods (Ag-In-Cd) and calcium being a major component of the concrete basemat in its oxide form (CaO). The phase diagram reported in the compilation of Moffatt [1981Mof] and reported by Baren [1988Bar] is based on investigations of Alexander *et al.* [1969Ale] using DTA, X-ray and metallography, and Pascal *et al.* [1970Pas] using DTA. Baar's results from thermal analysis [1911Baa] were reported by Hansen and Anderko [1958Han]. Six intermetallic stoichiometric compounds were clearly identified, Ag_9Ca_2, Ag_7Ca_2, Ag_2Ca, AgCa, Ag_3Ca_5, and $AgCa_3$. In addition, Calvert and Rand [1964Cal] identified Ag_8Ca_3 by X-ray analysis, but it was not confirmed by thermal analysis. Ag_7Ca_2 and AgCa melt congruently at 1004 K and 938 K, respectively, while the four others decompose peritectically. There is no reported mutual solubility of both elements in the solid state, and a complete miscibility in the liquid state. The thermodynamic properties of liquid alloys were electrochemically determined by Delcet and Egan [1978Del] and by Fischbach [1985Fis] using the Knudsen effusion technique. The enthalpy of formation of the compounds was measured potentiometrically [1981Not]. No experimental data are available for the thermodynamic properties of the other compounds. This system was assessed by Chevalier and Fischer [1996Che]. The excess Gibbs energy of the liquid and the Gibbs energy of the intermetallic compounds considered as stoichiometric ones were optimised from the selected experimental information. A sub-regular substitution model was used for the liquid. The enthalpy of formation was optimised in consistency with other data. The agreement with the experimental phase diagram information [1969Ale, 1970Pas] is quite satisfactory. The calculated activity of calcium at 1073 K is in satisfactory agreement with the experiments.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Ag,Ca)_1$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Ag,Ca)_1$
Ag_9Ca_2	⋯	⋯	⋯	⋯	AG9CA2	Ag_9Ca_2
Ag_7Ca_2	⋯	⋯	$hP18$	$P6_322$	AG7CA2	Ag_7Ca_2
Ag_2Ca	⋯	⋯	$oI12$	$Imma$	AG2CA	Ag_2Ca_1
AgCa	B_f	CrB	$oC8$	$Cmcm$	AGCA	Ag_1Ca_1
Ag_3Ca_5	$D8_1$	Cr_5B_3	$tI32$	$I4/mcm$	AG3CA5	Ag_3Ca_5
$AgCa_3$	⋯	⋯	⋯	⋯	AGCA3	$AgCa_3$
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	Ca_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Ca}			$\Delta_r H$ / (J/mol)
liquid $\rightleftharpoons$ Ag_7Ca_2	congruent	994.8	0.222	0.222		−13435
liquid + Ag_7Ca_2 $\rightleftharpoons$ Ag_9Ca_2	peritectic	961.4	0.167	0.222	0.182	−9076
liquid $\rightleftharpoons$ AgCa	congruent	929.4	0.500	0.500		−14074
liquid $\rightleftharpoons$ fcc + Ag_9Ca_2	eutectic	915.0	0.119	0.000	0.182	−11050
Ag_7Ca_2 + liquid $\rightleftharpoons$ Ag_2Ca	peritectic	861.6	0.222	0.341	0.333	−11746
liquid $\rightleftharpoons$ Ag_2Ca + AgCa	eutectic	838.5	0.388	0.333	0.500	−12503
AgCa + liquid $\rightleftharpoons$ Ag_3Ca_5	peritectic	829.6	0.500	0.630	0.625	−12107
liquid $\rightleftharpoons$ $AgCa_3$	congruent	756.7	0.750	0.750		−11010
liquid $\rightleftharpoons$ Ag_3Ca_5 + $AgCa_3$	eutectic	756.6	0.745	0.625	0.750	−11039
liquid $\rightleftharpoons$ $AgCa_3$ + bcc	eutectic	745.4	0.798	0.750	1.000	−10351
bcc $\rightleftharpoons$ $AgCa_3$ + fcc	degenerate	716.0	1.000	0.750	1.000	−929

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

x_{Ca}	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	−12625	−9184	2.703	−9184	0.000	0.000
0.200	−20995	−15698	4.161	−15698	0.000	0.000
0.300	−26244	−19779	5.079	−19779	0.000	0.000
0.400	−28785	−21661	5.596	−21661	0.000	0.000
0.500	−28918	−21581	5.763	−21581	0.000	0.000
0.600	−26899	−19775	5.596	−19775	0.000	0.000
0.700	−22944	−16478	5.079	−16478	0.000	0.000
0.800	−17222	−11926	4.161	−11926	0.000	0.000
0.900	−9795	−6355	2.703	−6355	0.000	0.000
1.000	0	0	0.000	0	0.000	0.000

Reference states: Ag(liquid), Ca(liquid)

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

x_{Ag}	ΔG_{Ag} [J/mol]	ΔH_{Ag} [J/mol]	ΔS_{Ag} [J/(mol·K)]	G^E_{Ag} [J/mol]	S^E_{Ag} [J/(mol·K)]	a_{Ag}	γ_{Ag}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−2489	−1374	0.876	−1374	0.000	0.790	0.878
0.800	−7544	−5182	1.855	−5182	0.000	0.490	0.613
0.700	−14727	−10952	2.966	−10952	0.000	0.249	0.355
0.600	−23620	−18213	4.247	−18213	0.000	0.107	0.179
0.500	−33830	−26493	5.763	−26493	0.000	0.041	0.082
0.400	−45020	−35321	7.619	−35321	0.000	0.014	0.036
0.300	−56968	−44225	10.010	−44225	0.000	0.005	0.015
0.200	−69769	−52734	13.382	−52734	0.000	0.001	0.007
0.100	−84747	−60375	19.145	−60375	0.000	0.000	0.003
0.000	−∞	−66678	∞	−66678	0.000	0.000	0.002

Reference state: Ag(liquid)

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

x_{Ca}	ΔG_{Ca} [J/mol]	ΔH_{Ca} [J/mol]	ΔS_{Ca} [J/(mol·K)]	G^E_{Ca} [J/mol]	S^E_{Ca} [J/(mol·K)]	a_{Ca}	γ_{Ca}
0.000	−∞	−105973	∞	−105973	0.000	0.000	0.000
0.100	−103844	−79473	19.145	−79473	0.000	0.000	0.001
0.200	−74798	−57763	13.382	−57763	0.000	0.001	0.004
0.300	−53118	−40374	10.010	−40374	0.000	0.007	0.022
0.400	−36532	−26833	7.619	−26833	0.000	0.032	0.079
0.500	−24006	−16670	5.763	−16670	0.000	0.104	0.207
0.600	−14818	−9411	4.247	−9411	0.000	0.247	0.411
0.700	−8362	−4586	2.966	−4586	0.000	0.454	0.648
0.800	−4086	−1724	1.855	−1724	0.000	0.680	0.850
0.900	−1468	−352	0.876	−352	0.000	0.871	0.967
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Ca(liquid)

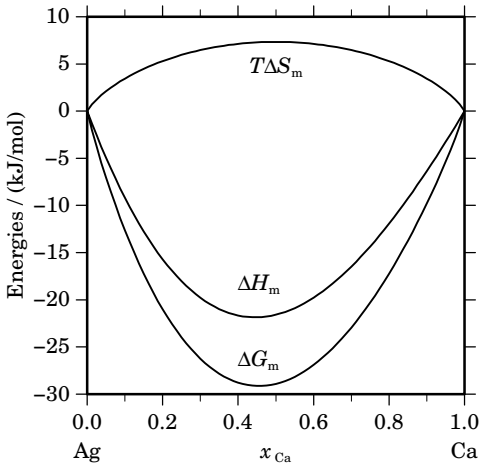

Fig. 2. Integral quantities of the liquid phase at T=1273 K.

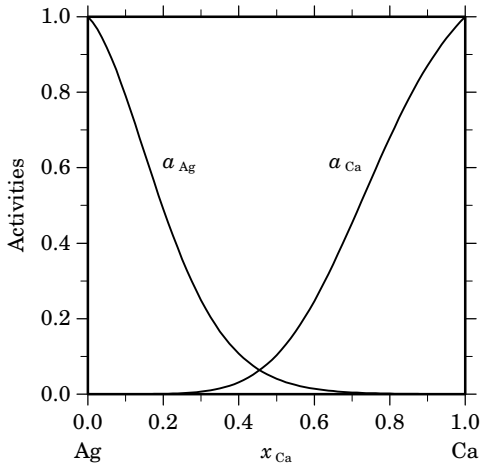

Fig. 3. Activities in the liquid phase at T=1273 K.

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

Compound	x_{Ca}	$\Delta_{\mathrm{f}}G^{\circ}$ / (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))
Ag_9Ca_2	0.182	−16462	−16583	−0.407	0.175
Ag_7Ca_2	0.222	−19522	−19671	−0.498	0.214
Ag_2Ca_1	0.333	−22563	−22786	−0.748	0.321
Ag_1Ca_1	0.500	−25291	−25626	−1.122	0.481
Ag_3Ca_5	0.625	−21322	−21740	−1.403	0.601
Ag_1Ca_3	0.750	−15106	−15608	−1.684	0.722

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