Ag – Cd (Silver – Cadmium)

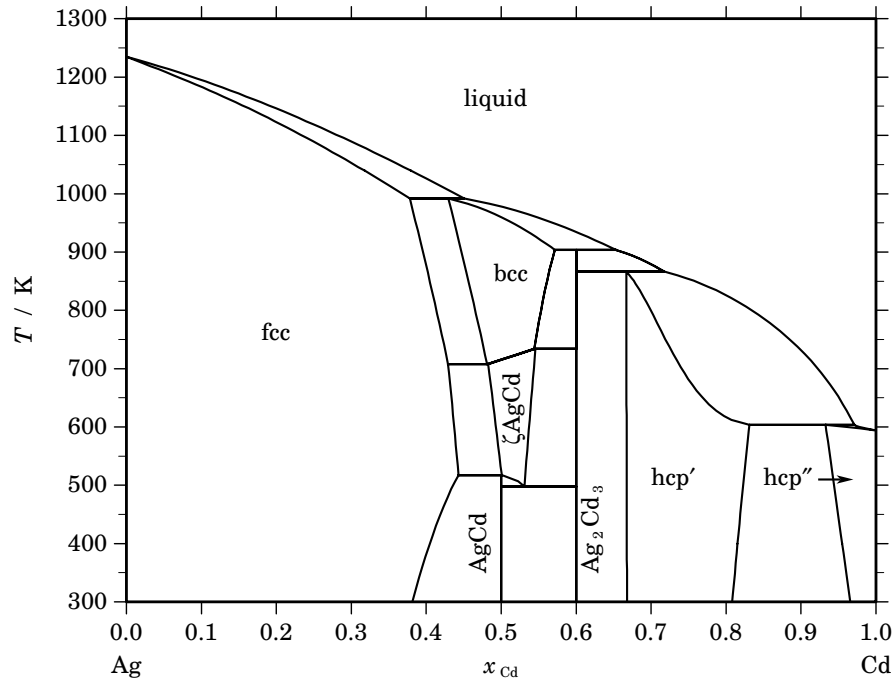

Fig. 1. Calculated phase diagram for the system Ag-Cd.

The Ag-Cd binary system contains two components interesting in the nuclear field, silver and cadmium being part of AIC control rods (Ag-In-Cd). The phase diagram has been reported in several compilations of binary systems [1958Han, 1965Ell, 1969Shu]. It is mainly based on the investigation of phase equilibria by [1905Ros, 1910Bru, 1911Pet, 1937Hum, 1939Owe] with additional results of [1896Gau, 1928Ast, 1928Nat, 1931Dur, 1935Dur, 1957Ray, 1959Pya, 1960Qua, 1962Mas]. The Ag-Cd system is a typical representative for the formation of intermetallic electron phases which are characterised by certain ratios of valence electrons to atoms. Among them are the β-, γ- and ϵ-brasses which are here denoted as the bcc, Ag_2Cd_3 and hcp$'$ phases, respectively. The latter hexagonal phase and the terminal Cd-rich solid solution (hcp$''$) have been modelled as a single hexagonal phase with a miscibility gap. A third hexagonal solid solution, ζAgCd, has been described as a separate phase. The intermetallic compounds AgCd and Ag_2Cd_3 have been approximated with stoichiometric descriptions. Ag_2Cd_3 has the γ-brass structure at higher temperature and a related superstructure at lower temperature but it has been described as a single phase only. The thermodynamic properties of liquid and solid alloys have been compiled from the literature in [1973Des] based on the measured activities of cadmium [1933Öla, 1942Sch, 1949Bir, 1956Her, 1956Sca, 1963Fil, 1969Con, 1970Mas, 1984Hou] and on calorimetric investigations [1956Kle, 1958And, 1958Orr, 1958Hul, 1969Wal]. This system has been assessed by Chevalier [2004Che]. A simple substitution model has been used for all solution phases (liquid, fcc, bcc, ζAgCd, and hcp) the excess interaction parameters being described by a Redlich-Kister polynomial of maximal second order. The heat capacity of the compounds was estimated from the pure solid components by using the Neumann-Kopp rule. The enthalpy and entropy of formation were optimised in consistency with other data. The agreement with the experimental information is quite satisfactory, as well for phase diagram [1905Ros, 1910Bru, 1911Pet, 1958Han, 1937Hum, 1939Owe] as thermodynamic data of solid and liquid phases (partial Gibbs energy and enthalpy of formation).

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Ag,Cd)_1$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Ag,Cd)_1$
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Ag,Cd)_1$
ζAgCd	$A3$	Mg	$hP2$	$P6_3/mmc$	AGCD_ZETA	$(Ag,Cd)_1$
AgCd	$B2$	CsCl	$cP2$	$Pm3m$	AGCD_B2	Ag_1Cd_1
Ag_2Cd_3	$D8_2$	Cu_5Zn_8	$cI52$	$I\overline{4}3m$	AG2CD3	Ag_2Cd_3
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(Ag,Cd)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Cd}			$\Delta_{\mathrm{r}}H$ / (J/mol)
fcc + liquid $\rightleftharpoons$ bcc	peritectic	991.8	0.378	0.450	0.430	−4390
bcc + liquid $\rightleftharpoons$ Ag_2Cd_3	peritectic	903.4	0.572	0.653	0.600	−2763
Ag_2Cd_3 + liquid $\rightleftharpoons$ hcp′	peritectic	866.6	0.600	0.717	0.667	−4172
bcc + Ag_2Cd_3 $\rightleftharpoons$ ζAgCd	peritectoid	734.4	0.544	0.600	0.546	−193
bcc $\rightleftharpoons$ fcc + ζAgCd	eutectoid	707.6	0.481	0.429	0.483	−206
hcp′ + liquid $\rightleftharpoons$ hcp″	peritectic	603.3	0.831	0.971	0.933	−4437
fcc + ζAgCd $\rightleftharpoons$ AgCd	peritectoid	516.9	0.443	0.501	0.500	−1030
ζAgCd $\rightleftharpoons$ AgCd + Ag_2Cd_3	eutectoid	497.8	0.531	0.500	0.600	−738

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

x_{Cd}	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	−5117	−3523	1.252	−1676	−1.451	0.000
0.200	−8006	−5993	1.582	−2710	−2.579	0.000
0.300	−9667	−7510	1.694	−3201	−3.385	0.000
0.400	−10376	−8177	1.727	−3252	−3.868	0.000
0.500	−10301	−8095	1.734	−2965	−4.030	0.000
0.600	−9564	−7365	1.727	−2440	−3.868	0.000
0.700	−8246	−6089	1.694	−1780	−3.385	0.000
0.800	−6382	−4369	1.582	−1085	−2.579	0.000
0.900	−3899	−2305	1.252	−458	−1.451	0.000
1.000	0	0	0.000	0	0.000	0.000

Reference states: Ag(liquid), Cd(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	−1454	−544	0.715	−339	−0.161	0.872	0.969
0.800	−3581	−2040	1.211	−1219	−0.645	0.713	0.891
0.700	−6213	−4284	1.515	−2438	−1.451	0.556	0.794
0.600	−9199	−7075	1.668	−3792	−2.579	0.419	0.699
0.500	−12416	−10210	1.734	−5080	−4.030	0.309	0.619
0.400	−15795	−13484	1.816	−6097	−5.803	0.225	0.562
0.300	−19384	−16695	2.112	−6640	−7.898	0.160	0.534
0.200	−23542	−19640	3.066	−6507	−10.316	0.108	0.541
0.100	−29867	−22116	6.089	−5495	−13.056	0.060	0.595
0.000	−∞	−23920	∞	−3401	−16.119	0.000	0.725

Reference state: Ag(liquid)

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

x_{Cd}	ΔG_{Cd} [J/mol]	ΔH_{Cd} [J/mol]	ΔS_{Cd} [J/(mol·K)]	G^E_{Cd} [J/mol]	S^E_{Cd} [J/(mol·K)]	a_{Cd}	γ_{Cd}
0.000	−∞	−40838	∞	−20319	−16.119	0.000	0.147
0.100	−38089	−30338	6.089	−13718	−13.056	0.027	0.274
0.200	−25708	−21805	3.066	−8673	−10.316	0.088	0.441
0.300	−17726	−15037	2.112	−4982	−7.898	0.187	0.625
0.400	−12141	−9829	1.816	−2442	−5.803	0.318	0.794
0.500	−8187	−5980	1.734	−850	−4.030	0.461	0.923
0.600	−5409	−3286	1.668	−3	−2.579	0.600	1.000
0.700	−3472	−1544	1.515	303	−1.451	0.720	1.029
0.800	−2092	−551	1.211	270	−0.645	0.821	1.026
0.900	−1014	−104	0.715	101	−0.161	0.909	1.010
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Cd(liquid)

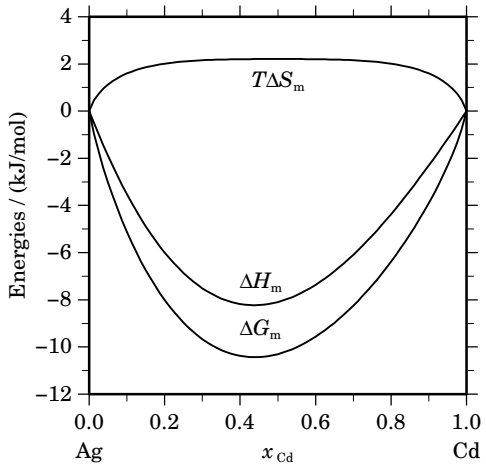

Fig. 2. Integral quantities of the liquid phase at T=1273 K.

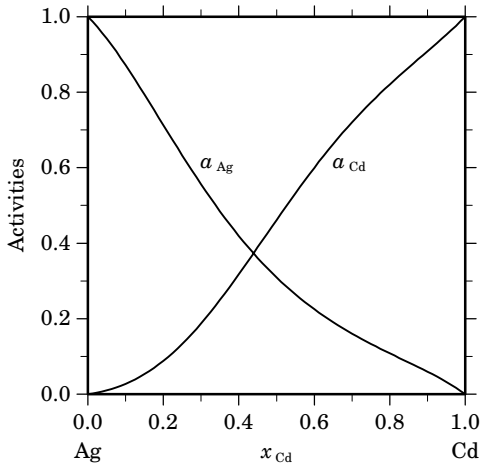

Fig. 3. Activities in the liquid phase at T=1273 K.

Table IVa. Integral quantities for the stable phases at 573 K.

Phase	x_{Cd}	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)]
fcc	0.000	0	0	0.000	0	0.000	0.000
	0.100	−4031	−2890	1.992	−2483	−0.710	0.038
	0.200	−6550	−4878	2.918	−4166	−1.243	0.076
	0.300	−8050	−6055	3.482	−5139	−1.597	0.114
	0.400	−8700	−6510	3.823	−5494	−1.773	0.152
	0.439	−8750	−6511	3.908	−5483	−1.794	0.167
ζAgCd	0.496	−8744	−6291	4.282	−5442	−1.481	0.000
	0.500	−8743	−6292	4.278	−5441	−1.486	0.000
	0.536	−8676	−6252	4.230	−5385	−1.513	0.000
Ag_2Cd_3	0.600	−8461	−6277	3.811			0.000
hcp′	0.667	−7885	−5944	3.387	−4854	−1.902	0.000
	0.700	−7499	−5686	3.164	−4589	−1.915	0.000
	0.800	−5396	−4004	2.429	−3012	−1.732	0.000
	0.829	−4665	−3403	2.203	−2483	−1.607	0.000
hcp″	0.936	−1878	−1197	1.188	−746	−0.787	0.000
	1.000	0	0	0.000	0	0.000	0.000

Reference states: Ag(fcc), Cd(hcp)

Table IVb. Partial quantities for Ag in the stable phases at 573 K.

Phase	x_{Ag}	ΔG_{Ag} [J/mol]	ΔH_{Ag} [J/mol]	ΔS_{Ag} [J/(mol·K)]	$G_{\mathrm{Ag}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Ag}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Ag}	γ_{Ag}
fcc	1.000	0	0	0.000	0	0.000	1.000	1.000
	0.900	−917	−466	0.787	−415	−0.089	0.825	0.917
	0.800	−2602	−1743	1.499	−1539	−0.356	0.579	0.724
	0.700	−4892	−3652	2.164	−3193	−0.802	0.358	0.512
	0.600	−7631	−6013	2.822	−5197	−1.425	0.202	0.336
	0.561	−8792	−7021	3.090	−6037	−1.717	0.158	0.282
ζAgCd	0.504	−8792	−6062	4.764	−5532	−0.925	0.158	0.313
	0.500	−8974	−6222	4.803	−5672	−0.961	0.152	0.304
	0.464	−10460	−7526	5.120	−6807	−1.256	0.111	0.240
Ag_2Cd_3	0.400	−10460	−6044	7.707			0.111	
	0.400	−13595	−9247	7.588			0.058	
hcp′	0.333	−13595	−9103	7.840	−8351	−1.311	0.058	0.173
	0.300	−17868	−13264	8.035	−12132	−1.975	0.024	0.078
	0.200	−25480	−20527	8.645	−17813	−4.737	0.005	0.024
	0.171	−26143	−21035	8.914	−17741	−5.749	0.004	0.024
hcp″	0.064	−26143	−19093	12.303	−13038	−10.568	0.004	0.065
	0.000	$-\infty$	−18991	∞	−10818	−14.262	0.000	0.103

Reference state: Ag(fcc)

Table IVc. Partial quantities for Cd in the stable phases at 573 K.

Phase	x_{Cd}	ΔG_{Cd} [J/mol]	ΔH_{Cd} [J/mol]	ΔS_{Cd} [J/(mol·K)]	G^E_{Cd} [J/mol]	S^E_{Cd} [J/(mol·K)]	a_{Cd}	γ_{Cd}
fcc	0.000	$-\infty$	−33703	∞	−29121	−7.995	0.000	0.002
	0.100	−32064	−24705	12.842	−21094	−6.303	0.001	0.012
	0.200	−22341	−17418	8.593	−14674	−4.789	0.009	0.046
	0.300	−15418	−11661	6.557	−9682	−3.453	0.039	0.131
	0.400	−10304	−7254	5.323	−5939	−2.295	0.115	0.288
	0.439	−8696	−5859	4.952	−4775	−1.891	0.161	0.367
ζAgCd	0.496	−8696	−6524	3.791	−5351	−2.047	0.161	0.325
	0.500	−8512	−6362	3.753	−5210	−2.011	0.168	0.335
	0.536	−7128	−5147	3.458	−4153	−1.735	0.224	0.418
Ag_2Cd_3	0.600	−7128	−6433	1.213			0.224	
	0.600	−5038	−4297	1.292			0.347	
hcp′	0.667	−5038	−4369	1.167	−3111	−2.196	0.347	0.520
	0.700	−3055	−2438	1.076	−1356	−1.889	0.527	0.752
	0.800	−375	126	0.875	688	−0.980	0.924	1.155
	0.829	−222	244	0.814	674	−0.750	0.954	1.152
hcp″	0.936	−222	24	0.429	93	−0.120	0.954	1.020
	1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Cd(hcp)

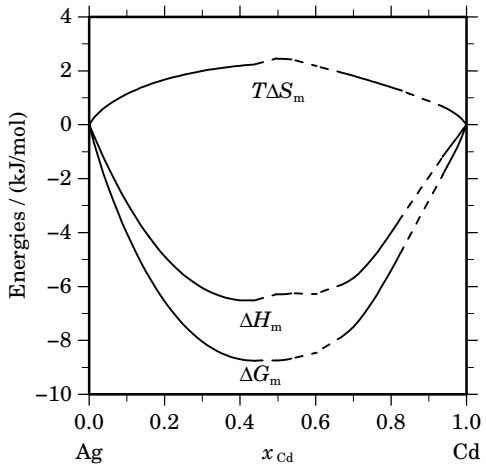

Fig. 4. Integral quantities of the stable phases at T=573 K.

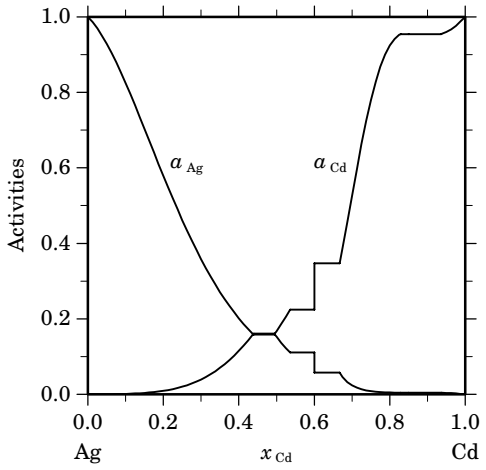

Fig. 5. Activities in the stable phases at T=573 K.

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

Compound	x_{Cd}	$\Delta_f G^\circ$ / (J/mol)	$\Delta_f H^\circ$ / (J/mol)	$\Delta_f S^\circ$ / (J/(mol·K))	$\Delta_f C^\circ_P$ / (J/(mol·K))
Ag_1Cd_1	0.500	−8005	−7325	2.279	0.000
Ag_2Cd_3	0.600	−7413	−6277	3.811	0.000

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