Pb – Pd (Lead – Palladium)

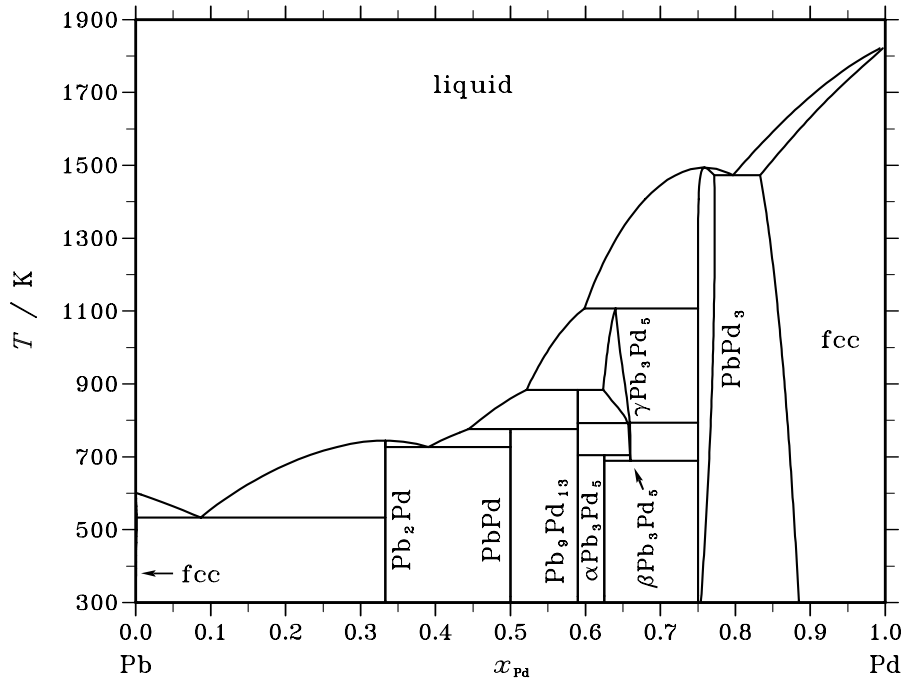

Fig. 1. Calculated phase diagram for the system Pb-Pd.

The Pb-Pd system displays extensive solid solubility of Pb in Pd and a number of peritectic reactions on moving from Pd- to Pb-rich alloys. These reactions lead to formation of several intermetallic phases, of which those denoted γPb_3Pd_5 and $PbPd_3$ show ranges of stoichiometry of about 3 at.%. The phases Pb_2Pd and $PbPd_3$ are reported to form congruently from the melt [86Mas]. The thermodynamic assessment of the system by Ghosh [99Gho] reproduces the features of the published phase diagram very closely, with only very small differences in the immediate vicinity of the Pb_3Pd_5 phase. Calculated enthalpies of mixing for the liquid phase are strongly exothermic and display a minimum close to the composition $PbPd_2$. Component activities display corresponding negative departures from ideality. The enthalpies of formation of the solid compound phases also become increasingly exothermic with increasing Pd content.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Pb,Pd)_1$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Pb,Pd)_1$
Pb_2Pd	$C16$	Al_2Cu	$tI12$	$I4/mcm$	C16_PDPB	Pb_2Pd_1
βPbPd	···	···	···	···	PDPB	Pb_1Pd_1
αPbPd	···	···	$aP32$	$P\overline{1}$	PDPB	Pb_1Pd_1
γPb_9Pd_{13}	···	···	···	···	PD13PB9	$Pb_{41}Pd_{59}$
βPb_9Pd_{13}	···	···	$hP5$	···	PD13PB9	$Pb_{41}Pd_{59}$
αPb_9Pd_{13}	···	···	$mC88$	$C2/c$	PD13PB9	$Pb_{41}Pd_{59}$
γPb_3Pd_5	···	···	···	···	PD5PB3_G	$Pd_1Pb_1(Pd,\Box)_1$
βPb_3Pd_5	$B8_1$	NiAs	$hP4$	$P6_3mc$	B81_PD5PB3	$Pd_1Pb_1(Pd,\Box)_1$
αPb_3Pd_5	···	···	$mC32$	$C2$	PD5PB3_A	Pd_4Pb_3
$PbPd_3$	$L2_1$	$AlCu_2Mn$	$cF16$	$Fm\overline{3}m$	L21_PD3PB	$Pd_3(Pb,Pd)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Pd}			$\Delta_{\mathrm{r}}H$ / (J/mol)
liquid $\rightleftharpoons$ $PbPd_3$	congruent	1494.0	0.759	0.759		−12203
liquid $\rightleftharpoons$ $PbPd_3$ + fcc	eutectic	1472.6	0.797	0.772	0.833	−9715
liquid + $PbPd_3$ $\rightleftharpoons$ γPb_3Pd_5	peritectic	1107.6	0.599	0.750	0.640	−4493
liquid + γPb_3Pd_5 $\rightleftharpoons$ Pb_9Pd_{13}	peritectic	884.0	0.521	0.624	0.590	−8460
γPb_3Pd_5 + $PbPd_3$ $\rightleftharpoons$ βPb_3Pd_5	peritectoid	793.8	0.659	0.750	0.660	−1801
γPb_3Pd_5 $\rightleftharpoons$ Pb_9Pd_{13} + βPb_3Pd_5	eutectoid	792.9	0.656	0.590	0.657	−2035
liquid + Pb_9Pd_{13} $\rightleftharpoons$ PbPd	peritectic	775.8	0.444	0.590	0.500	−5296
liquid $\rightleftharpoons$ Pb_2Pd	congruent	744.7	0.333	0.333		−7223
liquid $\rightleftharpoons$ Pb_2Pd + PbPd	eutectic	726.5	0.391	0.333	0.500	−7425
Pb_9Pd_{13} + βPb_3Pd_5 $\rightleftharpoons$ αPb_3Pd_5	peritectoid	704.3	0.590	0.659	0.625	−705
βPb_3Pd_5 $\rightleftharpoons$ αPb_3Pd_5 + $PbPd_3$	eutectoid	689.6	0.660	0.625	0.750	−988
liquid $\rightleftharpoons$ fcc + Pb_2Pd	eutectic	533.5	0.087	0.002	0.333	−5211

Table IIIa. Integral quantities for the liquid phase at 1873 K.

x_{Pd}	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	−8515	−7540	0.520	−3453	−2.182	0.000
0.200	−13648	−15064	−0.756	−5855	−4.917	0.000
0.300	−17103	−22385	−2.820	−7590	−7.899	0.000
0.400	−19365	−29070	−5.181	−8885	−10.777	0.000
0.500	−20598	−34434	−7.387	−9804	−13.150	0.000
0.600	−20737	−37543	−8.973	−10256	−14.568	0.000
0.700	−19504	−37213	−9.455	−9991	−14.534	0.000
0.800	−16391	−32010	−8.339	−8598	−12.500	0.000
0.900	−10572	−20250	−5.167	−5510	−7.870	0.000
1.000	0	0	0.000	0	0.000	0.000

Reference states: Pb(liquid), Pd(liquid)

Table IIIb. Partial quantities for Pb in the liquid phase at 1873 K.

x_{Pb}	ΔG_{Pb} [J/mol]	ΔH_{Pb} [J/mol]	ΔS_{Pb} [J/(mol·K)]	$G_{\mathrm{Pb}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Pb}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Pb}	γ_{Pb}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−2243	1	1.198	−602	0.322	0.866	0.962
0.800	−5294	−116	2.764	−1819	0.909	0.712	0.890
0.700	−8673	−1096	4.046	−3119	1.080	0.573	0.819
0.600	−12404	−4433	4.256	−4449	0.009	0.451	0.751
0.500	−17027	−12369	2.487	−6232	−3.276	0.335	0.670
0.400	−23635	−27898	−2.276	−9366	−9.894	0.219	0.548
0.300	−33974	−54761	−11.098	−15224	−21.109	0.113	0.376
0.200	−50721	−97450	−24.948	−25657	−38.330	0.039	0.193
0.100	−78850	−161205	−43.970	−42991	−63.115	0.006	0.063
0.000	$-\infty$	−252018	∞	−70027	−97.166	0.000	0.011

Reference state: Pb(liquid)

Table IIIc. Partial quantities for Pd in the liquid phase at 1873 K.

x_{Pd}	ΔG_{Pd} [J/mol]	ΔH_{Pd} [J/mol]	ΔS_{Pd} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Pd}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Pd}}$ [J/(mol·K)]	a_{Pd}	γ_{Pd}
0.000	$-\infty$	−75498	∞	−41454	−18.176	0.000	0.070
0.100	−64963	−75417	−5.581	−29105	−24.726	0.015	0.154
0.200	−47064	−74855	−14.838	−22000	−28.219	0.049	0.243
0.300	−36774	−72060	−18.839	−18024	−28.850	0.094	0.314
0.400	−29807	−66026	−19.337	−15538	−26.956	0.147	0.369
0.500	−24170	−56499	−17.261	−13376	−23.024	0.212	0.424
0.600	−18805	−43973	−13.438	−10850	−17.685	0.299	0.498
0.700	−13302	−29692	−8.751	−7748	−11.716	0.426	0.608
0.800	−7808	−15650	−4.187	−4333	−6.042	0.606	0.757
0.900	−2986	−4588	−0.855	−1345	−1.731	0.826	0.917
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Pd(liquid)

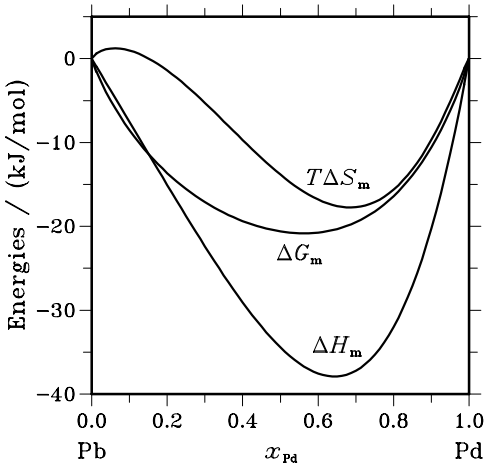

Fig. 2. Integral quantities of the liquid phase at T=1873 K.

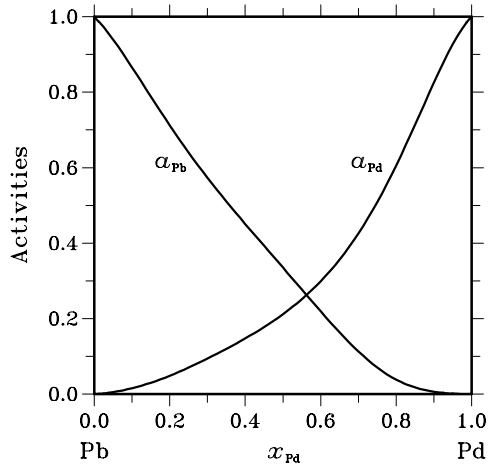

Fig. 3. Activities in the liquid phase at T=1873 K.

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

Phase	x_{Pd}	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)]
liquid	0.000	0	0	0.000	0	0.000	0.000
	0.100	−7748	−6190	1.224	−4307	−1.479	0.583
	0.200	−13192	−12363	0.651	−7895	−3.510	1.166
	0.300	−17431	−18335	−0.710	−10965	−5.789	1.749
	0.400	−20655	−23669	−2.368	−13532	−7.964	2.331
	0.500	−22757	−27683	−3.870	−15420	−9.633	2.914
	0.600	−23392	−29442	−4.753	−16269	−10.348	3.497
	0.634	−23179	−29323	−4.826	−16228	−10.287	3.696
$PbPd_3$	0.750	−22024	−37000	−11.764	−16073	−16.439	0.000
	0.772	−20803	−33868	−10.263	−15126	−14.722	0.000
fcc	0.848	−15895	−23365	−5.868	−11375	−9.418	0.000
	0.900	−11871	−16910	−3.959	−8430	−6.661	0.000
	1.000	0	0	0.000	0	0.000	0.000

Reference states: Pb(liquid), Pd(fcc)

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

Phase	x_{Pb}	ΔG_{Pb} [J/mol]	ΔH_{Pb} [J/mol]	ΔS_{Pb} [J/(mol·K)]	$G_{\mathrm{Pb}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Pb}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Pb}	γ_{Pb}
liquid	1.000	0	0	0.000	0	0.000	1.000	1.000
	0.900	−1524	1	1.198	−409	0.322	0.866	0.962
	0.800	−3635	−116	2.764	−1273	0.909	0.709	0.887
	0.700	−6246	−1096	4.046	−2471	1.080	0.554	0.792
	0.600	−9851	−4433	4.256	−4444	0.009	0.394	0.657
	0.500	−15535	−12369	2.487	−8198	−3.276	0.230	0.461
	0.400	−25001	−27898	−2.276	−15302	−9.894	0.094	0.236
	0.366	−29491	−35566	−4.772	−18851	−13.130	0.062	0.168
$PbPd_3$	0.250	−29499	−141869	−88.272	−14821	−99.802	0.062	0.247
	0.228	−71287	−142992	−56.328	−55619	−68.635	0.001	0.005
fcc	0.152	−71287	−115071	−34.395	−51381	−50.031	0.001	0.008
	0.100	−91557	−141198	−38.995	−67185	−58.140	0.000	0.002
	0.000	$-\infty$	−201522	∞	−104324	−76.353	0.000	0.000

Reference state: Pb(liquid)

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

Phase	x_{Pd}	ΔG_{Pd} [J/mol]	ΔH_{Pd} [J/mol]	ΔS_{Pd} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Pd}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Pd}}$ [J/(mol·K)]	a_{Pd}	γ_{Pd}
liquid	0.000	$-\infty$	−61997	∞	−47812	−11.143	0.000	0.011
	0.100	−63764	−61915	1.452	−39393	−17.693	0.002	0.024
	0.200	−51419	−61354	−7.804	−34384	−21.186	0.008	0.039
	0.300	−43530	−58558	−11.806	−30787	−21.816	0.016	0.055
	0.400	−36862	−52525	−12.304	−27164	−19.922	0.031	0.077
	0.500	−29979	−42998	−10.227	−22642	−15.990	0.059	0.118
	0.600	−22320	−30472	−6.404	−16913	−10.651	0.121	0.202
	0.634	−19536	−25720	−4.857	−14714	−8.646	0.158	0.249
$PbPd_3$	0.750	−19534	−2066	13.721	−16491	11.331	0.158	0.211
	0.772	−5928	−1714	3.310	−3195	1.163	0.571	0.739
fcc	0.848	−5928	−6864	−0.735	−4177	−2.111	0.571	0.674
	0.900	−3017	−3100	−0.066	−1902	−0.942	0.752	0.836
	1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Pd(fcc)

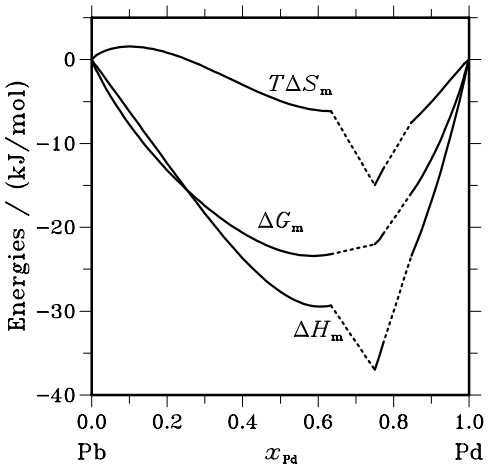

Fig. 4. Integral quantities of the stable phases at T=1273 K.

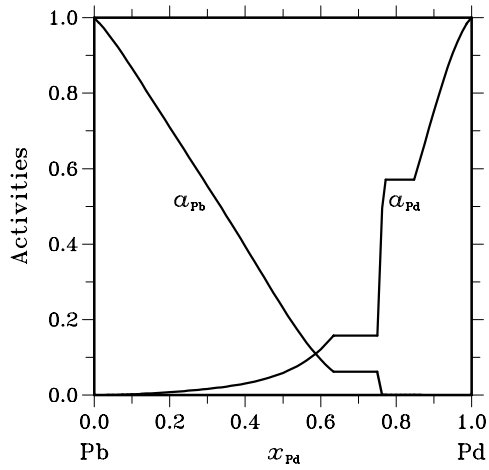

Fig. 5. Activities in the stable phases at T=1273 K.

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

Compound	x_{Pd}	$\Delta_{\mathrm{f}}G^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}H^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}S^{\circ}$ / (J/(mol·K))	$\Delta_{\mathrm{f}}C^{\circ}_{P}$ / (J/(mol·K))
Pb_2Pd_1	0.333	−22990	−24835	−6.190	0.000
Pb_1Pd_1	0.500	−31694	−35326	−12.182	0.000
Pb_9Pd_{13}	0.590	−35598	−40057	−14.957	0.000
αPb_3Pd_5	0.625	−35197	−39445	−14.249	0.000
$PbPd_3$	0.750	−32894	−35804	−9.761	0.000

References

[86Mas] T.B. Massalski (ed.): Binary Alloy Phase Diagrams, ASM, Metals Park, Ohio, 1986.
[99Gho] G. Ghosh: J. Phase Equilibria **20** (1999) 309–315.