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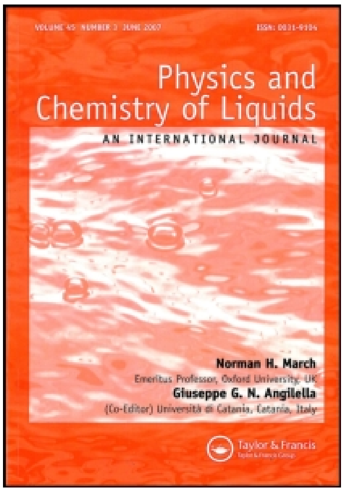

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THERMODYNAMIC INVESTIGATION OF THE Pd-Pb BINARY LIQUID ALLOYS

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The enthalpy of formation, h^f, of the Pd-Pb alloys was measured by direct reaction calorimetry (drop method) at 840 K and 1344 K. At 840 K the results are in good agreeement with those obtained previously between 922 and 1154 K (no temperature dependence). At 1344 K, they confirm that the enthalpy of formation of the liquid phase increases with increasing temperature above 1154 K (as previously observed at 1240 K). The crystallization of Pd_3Pb was observed and we can deduce its enthalpy of formation.

The strong negative departures from ideality of the thermodynamic behaviour of the melt ($h^f_{min} = -40$ kJ mol^{-1}, $C_p^{XS} > 0$ at high temperature) correspond undoubtedly to the presence of chemical short-range order. A "short-range order-disorder transition" begins between 1154 and 1240 K. In order to apply the regular associated solution model we calculated the free enthalpy of formation of the liquid phase from the phase diagram and the thermodynamic functions of formation of the solid intermediate compounds. The application of the model allowed us to explain the behaviour of the Pd-Pb melts by the existence of two kinds of associate i.e. Pd_2Pb and PdPb.

KEY WORDS: Enthalpy of formation, chemical short-range order.

1. INTRODUCTION

The phase diagram of the system investigated is shown on Figure 1 from Moffatt[1]. According to Marcotte[2] and Ellner *et al.*[3] it exhibits five intermediate compounds i.e. Pb_2Pd, PbPd, Pb_9Pd_{13}, Pb_3Pd_5 and $PbPd_3$. The first and the last ones only melt congruently. We measured recently[4] the enthalpy of formation, h^f, of the liquid Pb-Pd alloys at six temperatures (623, 750, 822, 921, 1154 and 1240 K) by direct reaction calorimetry (drop method, successive additions of pure Pd to the liquid bath). h^f is strongly negative in the whole range of concentration ($h^f_{min} = -38.4$ kJ·mol^{-1} for $x_{Pd} = 0.665$) and does not depend on temperature up to 1154 K. However at 1240 K the enthalpy of mixing becomes somewhat less negative but at such a high temperature the problem of eventual losses of lead by evaporation arises since the determinations were performed at the beginning by addition of palladium in pure liquid lead (during the two hours needed to reach the thermal equilibrium of the calorimetric cell there was pure lead in the crucible). Thus we carried out the measurement of the enthalpy of mixing at high temperature (1344 K) by the same method[5] but adding pure lead on solid palladium. Then the activity of lead was strongly decreased by

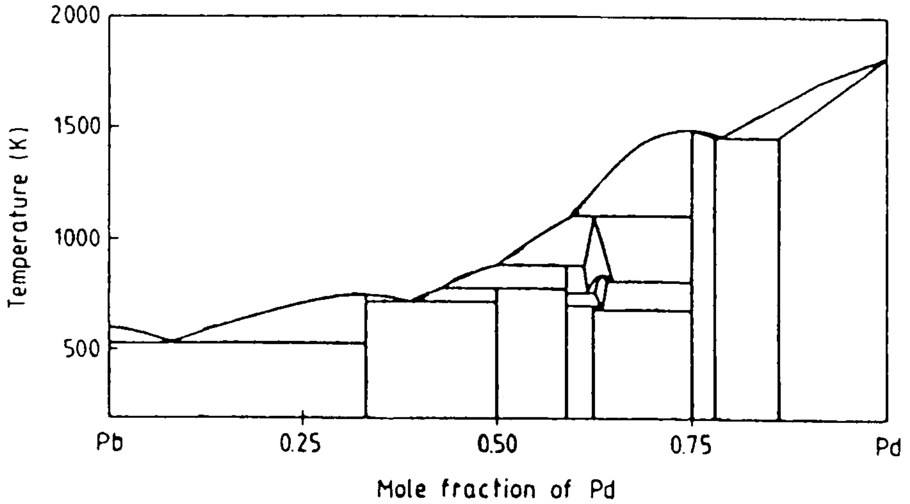

Figure 1 Phase diagram of the Pd-Pb system according to Moffatt *et al.*[1]

alloying and we avoid any evaporation of lead. Furthermore, we tried to determine in this way the enthalpy of formation of the Pd_3Pb compound since we pointed out in our previous paper that adding pure Pd to the saturated melt did not lead to the precipitation of any compound. Finally, in order to check our previous results we measured also the enthalpy of formation at 840 K i.e. in a range where no temperature dependence was observed by additions of Pd in pure Pb.

2. CALORIMETRIC METHOD

The apparatus employed were high-temperature Calvet-calorimeters ($T/K < 1400$) built in the lab. The drop method used (direct reaction calorimetry) has been already described[5]. The enthalpy of formation at 1344 K was deduced from the heat effects corresponding to successive additions of small quantities of Pb (from about 20 to 50 mg according to the concentration range) at T_0 (near 298 K) into a Pd_xPb_{1-x} binary alloy placed in an alumina crucible at the bottom of the calorimetric cell at 1344 K. Before the first addition of Pb, the melt was pure solid Pd (about 200 mg). Thus each small quantity of lead added to the alloy corresponded to the heating of lead from T_0 to T (including the melting process) and to the diffusion of lead into solid Pd. Then the sum of the successive thermal effects corresponds to the reaction:

$$x\,\mathrm{Pb(cr}, T) + (1-x)\mathrm{Pd(cr, 298\,K)} \rightarrow \mathrm{Pd}_x\mathrm{Pd}_{1-x}(\mathrm{cr\ or\ l}, T) \qquad (1)$$

They lead to the integral enthalpy of formation of the alloys with respect to composition. At 840 K, the measurements were performed like in our previous work[4], adding pure Pd to pure liquid Pb. The pure metals used were purchased from Koch-Light with metallic impurities less than 10^{-3} mass%. The calibration data were performed by adding some small pieces of α-alumina of well-known enthalphy[6]. The values of the heat content from T_0 to T and the enthalpy of melting of Pb needed to change the reference state from Pb(T_0cr) to Pb(T, l) were derived from Hultgren *et al.*[7]

3. EXPERIMENTAL RESULTS

The two series of results obtained at 840 K are given Table 1 and shown on Figure 2. They agree well with our previous results: there is no temperature dependence below 1154 K. As already mentioned, the PdPb intermediate compound does not precipitate when Pd is added to a saturated melt. For a mole fraction of Pd, $x_{Pd} > 0.47$, the heat effects due to further additions of Pd corresponds only to heating of the samples from 298 to 840 K. However, $x_{Pd} = 0.47$ agrees well with the phase boundary deduced from Moffatt. When referred to liquid Pb and liquid Pd, the extrapolation of the straight line of Figure 2 yields the enthalpy of cristallization of pure Pd. We tried to obtain the equilibrium state (i.e. a liquid + PdPb two-phase state) for a sample corresponding to solid Pd (about 20 mg) in a saturated liquid by annealing it at 840 K for 24 hours. We did not observed any dissolution of solid Pd.

The results obtained at 1344 K are listed in Table 2 and shown on Figure 3. The enthalpy of formation shows two breaks with respect to composition. It shows that adding liquid Pb to solid Pd leads to the formation of the Pd_3Pb intermediate compound which is not the case adding solid Pd to liquid Pb. The first break ($x_{Pd} = 0.664$) corresponds to the boundary between the liquid phase and the Pd_3Pb + liquid two-phase domain (where the enthalpy of formation shows a linear dependence versus concentration). The second one corresponds to the pure Pd_3Pb solid compound. The two boundaries agree well with the phase diagram selected by Moffatt. The enthalpy of formation of Pd_3Pb is −50.0 kJ per mole of metal referred to both pure liquid components.

Table 1 Molar integral enthalpy of formation of the Pd-Pb alloys at 840 K referred to both liquid components with respect to the mole fraction of Pd.

x_{Pd}	Δh^f (kJ/mol)	x_{Pd}	Δh^f (kJ/mol)
0.124	−9.72	0.116	−9.20
0.261	−18.78	0.220	−15.90
0.361	−25.21	0.320	−22.30
0.437	−29.88	0.380	−26.50
0.491	−30.57	0.405	−28.11
0.547	−29.08	0.470	−31.22
0.584	−28.19	0.500	−30.23
0.633	−27.15	0.576	−29.31
		0.650	−27.80
		0.692	−25.71

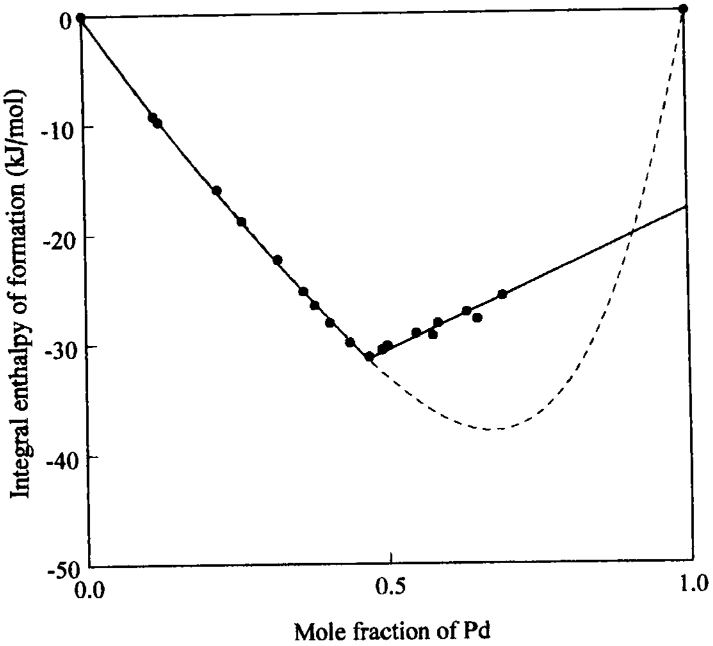

Figure 2 Molar integral enthalpy of formation of the Pd-Pb alloys at 840 K referred to both liquid components versus mole fraction of Pd. ●: Experimental, ——: Smoothed, ...: Extrapolated.

Table 2 Molar integral enthalpy of formation of the Pd-Pb alloys at 1344 K referred to both liquid components with respect to the mole fraction of Pd.

x_{Pb}	Δh^f (*kJ/mol*)	x_{Pb}	Δh^f(*kJ/mol*)	x_{Pb}	Δh^f(*kJ/mol*)
0.33	−33.88	0.38	−34.24	0.32	−36.31
0.40	−33.81	0.43	−33.23	0.38	−33.90
0.44	−32.84	0.46	−31.97	0.40	−33.69
0.48	−31.47	0.53	−28.73	0.43	−32.81
0.53	−29.29	0.60	−25.82	0.45	−32.23
0.56	−27.95			0.49	−30.93
		0.11	−31.97	0.51	−29.74
0.13	−34.85	0.14	−36.30	0.56	−27.67
0.21	−48.79	0.19	−44.24	0.58	−26.50
0.28	−46.51	0.25	−50.36		
0.35	−34.50	0.28	−44.52		

Figure 4 shows the enthalpy of formation of the Pd-Pb melts at different temperatures with reference to pure liquid components. Up to 1154 K, h^f does not depend on temperature. We can assume:

$$h^f(x_{Pd})/\mathrm{kJ\ mol^{-1}} = x_{Pd}(1 - x_{Pd})(-83.722 + 1.783\ x_{Pd} - 201.07\ x_{Pd}^2) \qquad (2)$$

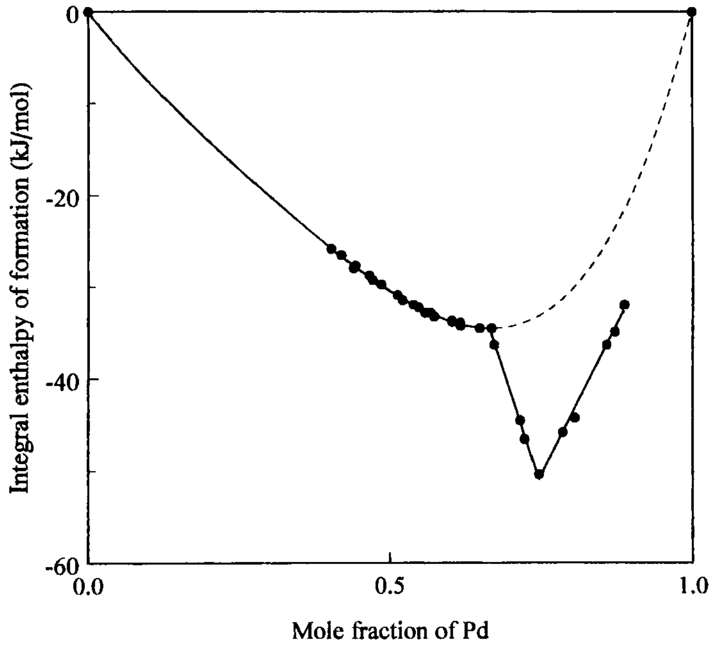

Figure 3 Molar integral enthalpy of formation of the Pd-Pb alloys at 1344 K referred to both liquid components versus mole fraction of Pd. ●: Experimental, ——: Smoothed, ...: Extrapolated.

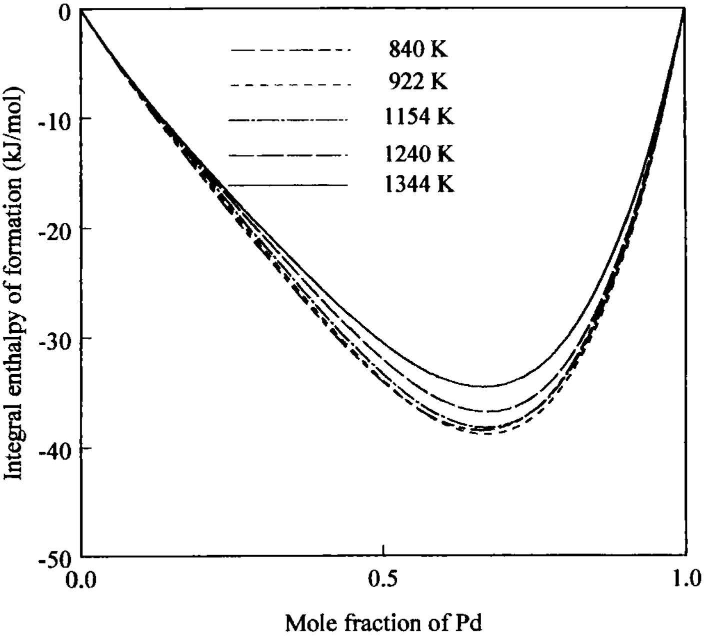

Figure 4 Molar integral enthalpy of formation of the Pd-Pb liquid alloys at different temperatures referred to both liquid components versus mole fraction of Pd.

Above 1154 K, h^f increases with increasing temperature and can be given by the following expression:

$$h^f(x_{\mathrm{Pd}})/\mathrm{kJ\ mol^{-1}} = x_{\mathrm{Pd}}(1 - x_{\mathrm{Pd}}) \sum_i (a_i - c_i T - d_i T^2) x_{\mathrm{Pd}}^i \qquad (3)$$

with a_i, c_i and d_i listed in Table 3.

At any temperature, the enthalpic minimum is located close to $x_{\mathrm{Pd}} = 0.667(\mathrm{Pd_2Pb})$ but, up to now, the minimum was determined only by extrapolation from lower mole fraction data. At 1344 K the minimum was reached in agreement with our previous determinations. For $x_{\mathrm{Pd}} = 0.667$, the average excess heat capacity is positive (19.11 and 17.83 J·mol^{-1}·K^{-1} between 1154 and 1240 K and between 1240 and 1344 K respectively).

4. CALCULATION OF THE FREE ENTHALPY OF FORMATION OF THE MELTS

The activity of Pb, a_{Pb}, in the Pd-Pb melts were already reported in three papers. Schwerdtfeger[8] and Vassiliev *et al.*[9] determined a_{Pb} from electromotive-force measurements in the temperature ranges 1123–1473 K and 1050 and 1123 K respectively. Sommer *et al.*[1] derived a_{Pb} from the vapor pressure of Pb measured from 950 to 1050 K by an effusion method. At 1050 K the results of Vassiliev *et al.* agree with those of Sommer *et al.* only for $x_{\mathrm{Pd}} < 0.3$ whereas at 1123 K they are in agreement with those of Schwerdtfeger only around $x_{\mathrm{Pd}} = 0.5$. The use of such a_{Pb} data to calculate the integral molar free enthalpy of formation of the melt, g^f, leads to large descrepancies. Then, since we needed accurate values of g^f in order to apply the regular associated solution models and to elucidate the nature and stability of the short-range order of the liquid alloys, we calculated the free enthalpy of formation from the experimental phase diagram, the experimental enthalpy of formation of the liquid and the free enthalpy of formation of the solid compounds[11]. The results obtained in this way can be fitted according to the following equations.:

$$g^{f,\mathrm{xs}}/\mathrm{kJ\ mol^{-1}} = x(1-x)(-65.93 - 13.41x - 1024.9x^2 + 5454.4x^3 - 12917x^4 + 11526x^5) \quad \text{for} \quad 0 < x_{\mathrm{Pd}} < 0.5 \qquad (4)$$

Table 3 Coefficients of the Eqn. (3).

i	a_i	c_i	$d_i\,10^5$
1	−80.951	0.008739	−0.432
2	−39.346	0.007381	−4.9
3	41.614	0.303713	−6.3
4	−122.784	−0.090552	−3.2

$$g^{f,\mathrm{xs}}/\mathrm{kJ\ mol}^{-1} = x(1-x)(-154.61 + 138.70x - 254.90x^2 + 75.33x^3) \quad \text{for} \quad 0.5 < x_{\mathrm{Pd}} < 1 \tag{5}$$

The results at 1154 K are listed in Table 4 and shown in Figure 5. As for h^f, the minimum is located near $x_{\mathrm{Pd}} = 0.67$ (-34.1 kJ mol^{-1}). When used to recalculate the phase boundaries around the Pb-rich eutectic and the $PdPb_2$ and Pd_3Pb compounds they give a good agreement with the experimental phase diagram (Fig. 6). The values of the partial free enthalpy of Pb derived from our data are compared with those of Vassiliev *et al.* and those of Schwerdtfeger in Figure 7. The agreement is good with Vassiliev *et al.* Since Sommer *et al.* did not report any

Table 4 Excess molar integral free enthalpy of formation of the Pd-Pb liquid alloys at 1154 K referred to both liquid components with respect to the mole fraction of Pd.

x_{Pd}	g^f (*kJ/mol*)	x_{Pd}	g^f(*kJ/mol*)
0.10	−6.710	0.60	−33.937
0.20	−12.735	0.70	−33.444
0.30	−18.774	0.80	−27.505
0.40	−24.949	0.90	−15.763
0.50	−30.499		

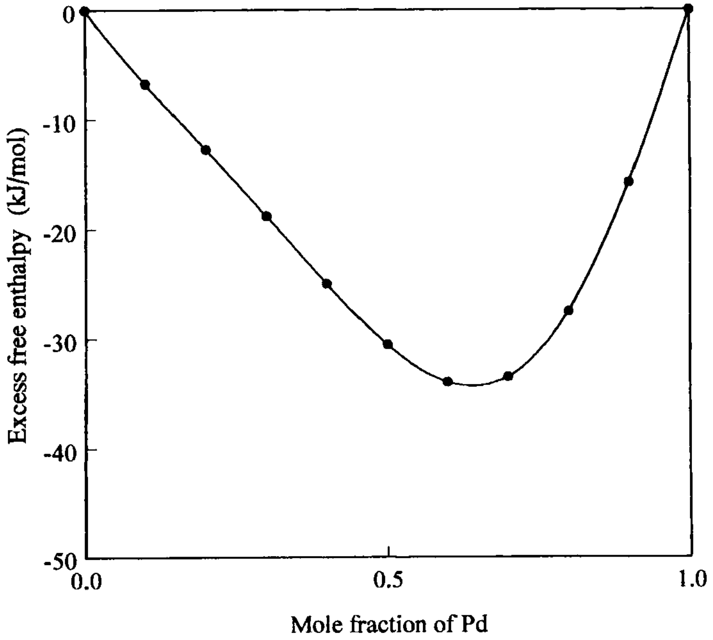

Figure 5 Excess molar integral free enthalpy of formation of the Pd-Pb liquid alloys at 1154 K referred to both liquid components versus mole fraction of Pd. ●: Experimental, ——: Smoothed.

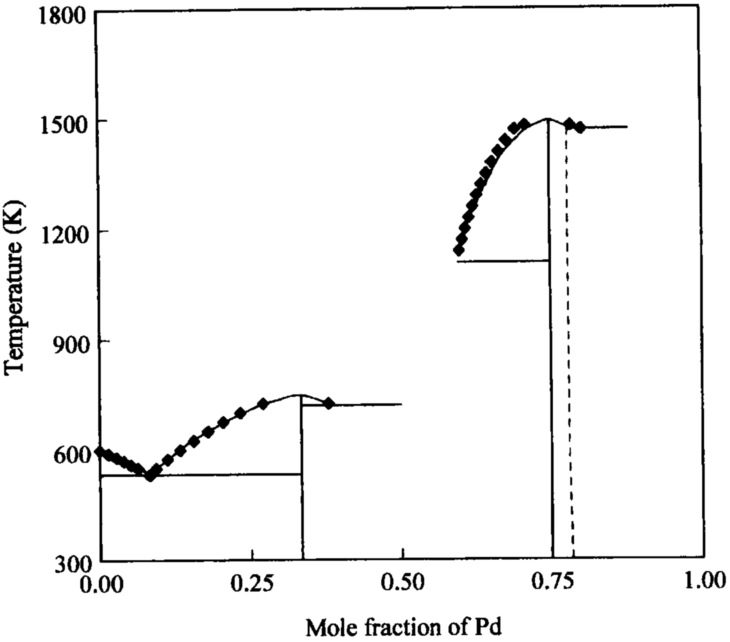

Figure 6 Parts of the Pd-Pb phase diagram used to calculate the free enthalpy of formation ——: Used for calculation of the free enthalpy of the liquid phase ● : Recalculated from the thermodynamic functions of the liquid and solid phases.

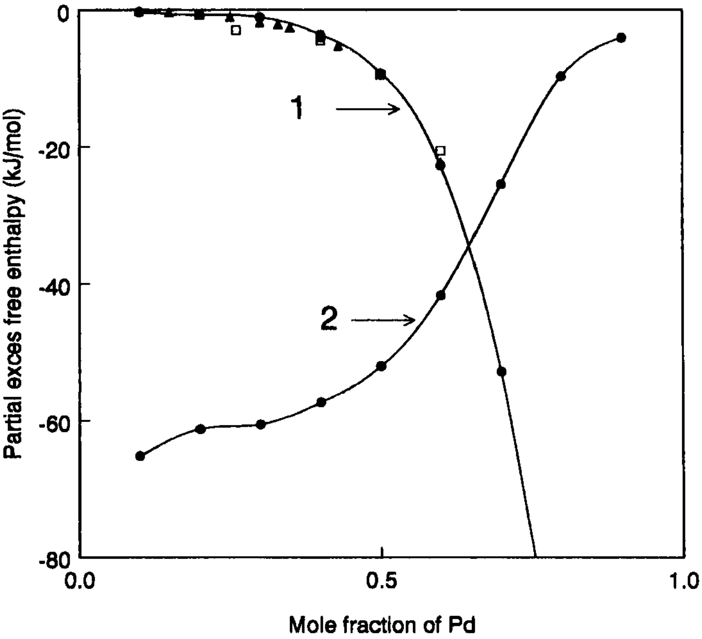

Figure 7 Molar partial free enthalpy of Pb (curve 1) and Pd (curve 2) at 1154 K referred to pure liquid Pb and Pd versus mole fraction of Pd. ●: Calculated from the phase diagram (this work) □: According to Schwerdfeger[8] ▲: According to Vassiliev *et al.*[9]

numerical data but only a small figure it was not possible to derive the partial functions.

5. APPLICATION OF THE REGULAR ASSOCIATED SOLUTION MODEL

From the enthalpy and free enthalpy of formation of the melt in the whole range of concentration we can applied the regular associated solution model (12–14) to the liquid phase in order to elucidate the nature and the stability of the associations. The location of the minima of the h^f and g^f very close to $x_{Pd} = 0.67$ suggests that Pd_2Pb clusters play an important role in the chemical short-range order. However, the assumption of only Pd_2Pb associates in the melt did not allow us to reproduce correctly the thermodynamic functions of formation of the liquid. Then, we tried to fit h^f and g^f assuming two kinds of clusters as we did for the Pd-Ge and Pt-Ge melts[15]. The fit between experimental data and calculated ones was the best assuming Pd_2Pb and PdPb:

$$2Pd + Pb \Leftrightarrow Pd_2Pb \quad \Delta H^\circ = -117.0\,\mathrm{kJ\cdot mol^{-1}}, \quad \Delta S^\circ = -9.7\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}} \tag{6}$$

$$Pd + Pb \Leftrightarrow PdPb \quad \Delta H^\circ = -69.7\,\mathrm{kJ\cdot mol^{-1}}, \quad \Delta S^\circ = 3.3\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}} \tag{7}$$

and two kinds of interactions (Pd-Pd_2Pb with a parameter equal to $-77.6\,\mathrm{kJ\cdot mol^{-1}}$ and Pb-PdPb with a parameter equal to $0.04\,\mathrm{kJ\cdot mol^{-1}}$). The thermodynamic contributions due to the interactions between Pb and PdPb can be neglected. As shown by Figure 8, the values of h^f and g^f measured and calculated according to the model are in good agreement.

6. CONCLUSION

The thermodynamic behaviour of the Pd-Pb melts is characterized by strong negative departures from ideality since its enthalpy of formation show a minimum of about $-40\,\mathrm{kJ\cdot mol^{-1}}$ for $x_{Pd} = 0.67$. The minimum does not depend on temperature from 821 to 1154 K but decreases when temperature increases above 1154 K (see Fig. 4). Its location remains unchanged. Such a behaviour means undoubtedly that the chemical short-range order (CSRO) of the melt, responsible for the negative departures from ideality, begins to be destroyed between 1154 and 1240 K by thermal agitation. Between 1154 and 1240 K begins what we called[13] "*short-range order-disorder transition*".

In order to determine the nature of the CSRO, we applied the regular associated solution model to the system. For that, we needed accurate values of the free enthalpy of formation of the liquid. The model lead to the existence of a complex CSRO i.e. two kinds of associates (Pd_2Pb and PdPb), like for the Pd-Ge and Pt-Ge

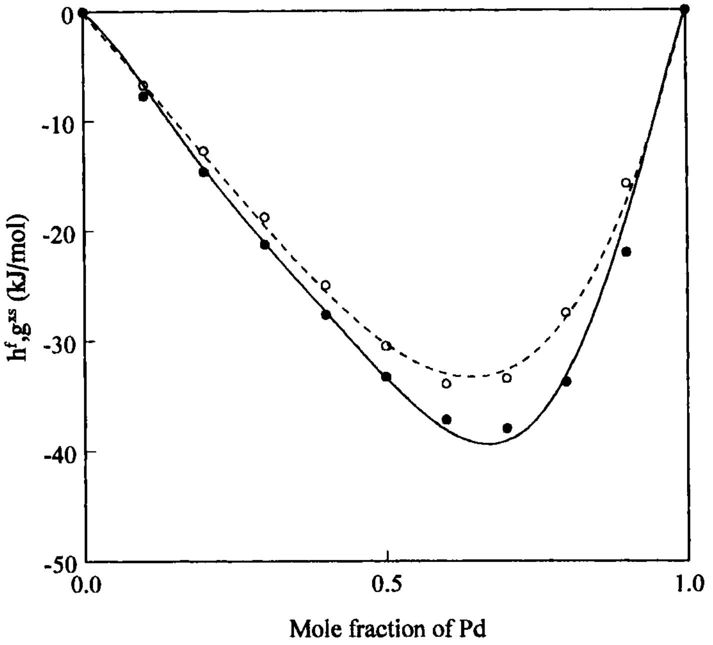

Figure 8 Molar integral thermodynamic functions of formation of the Pd-Pb liquid alloys at 1154 K referred to both liquid components versus mole fraction of Pd. h^f: ○ (experimental data), ...: according to the regular associated solution model. g^f: ● (calculated from h^f and the phase diagram), ——: according to the regular associated solution model.

binaries[15]. Their standard enthalpies of formation are close to each other when referred to a mole of metal (respectively -39.0 and -34.8 kJ·mol^{-1}). However, in the case of Pd-Ge and Pd-Ge systems the minima of h^f were located between the stoichiometries of the two kinds of associates whereas here the minima corresponds to Pd_2Pb.

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