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Thermodynamic investigation of Pt–Ge and Pd–Ge binary alloys

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Abstract

The enthalpy of formation, ΔH_f, of Pt–Ge and Pd–Ge alloys was measured in the temperature range 1270–1680 K with respect to composition by direct reaction calorimetry (drop method) with the help of high temperature Calvet-type calorimeters. The results agree well with our previous measurements. The enthalpies of formation and melting of the PtGe and Pd_2Ge intermediate phases were also obtained. Furthermore, we determined also some phase boundaries from the breaks of the $\Delta H_f(x)$ curves in agreement with the published phase diagram.

From our enthalpy data and those of the free enthalpy of formation of the melts determined by Knudsen cell effusion mass spectrometry we were able to derive also the thermodynamic properties of PtGe and Pd_2Ge at their melting points. These lead to the calculation of solid compound–liquid domains in agreement with the published ones and our experimental determinations.

The thermodynamic behaviour of the two melts is characterized by strong negative deviations to ideality, suggesting strong chemical short-range order. The stoichiometries of the associates are strongly connected with the highest melting intermediate compounds of both binaries, *i.e.* Pd_2Ge and PtGe. Their stability seems very high, since the excess heat capacities of the liquid phases are particularly low. Such a conclusion is in agreement with the low values of the entropy of melting of the compounds when compared with those deduced from additivity.

1. Introduction

The phase diagrams of the two systems investigated are well known (Figs. 1 and 2 according to Oya and Suzuki [1] for Pt–Ge and Khalaff and Schubert [2] for Pd–Ge). Among several intermediate phases, they exhibit the same compounds with 2:1 and 1:1 molar ratios, but Pd_2Ge melts at a higher temperature than PdGe (1568 instead of 1103 K) whereas it is the reverse situation for Pt_2Ge and PtGe (1068 and 1343 K respectively) according to Moffatt [3]. Moreover, according to Oya and Suzuki [1], Pt_2Ge decomposes peritectically, since it melts congruently according to Jain and Bhan [4].

The enthalpies of formation, ΔH_f, of Pt–Ge and Pd–Ge alloys have been determined by direct reaction calorimetry (drop method) by Castanet [5] at 1273 and 1352 K (Pt–Ge) and 1273 K (Pd–Ge). The Gibbs energies of formation of both binaries have been determined at 2053 and 1820 K respectively by Castanet and Chastel [6] by Knudsen cell effusion combined with mass spectrometry. The strong negative departure from ideality and the location of the extrema of the enthalpy of formation with respect to composition imply the existence of chemical short-range order correlated with the congruently melting compounds of the systems.

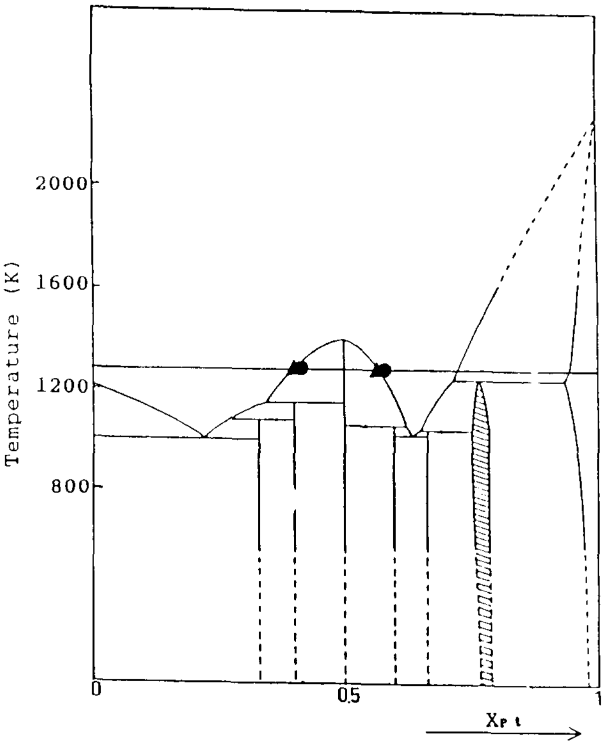

Fig. 1. Phase diagram of the Pt–Ge system according to Oya and Suzuki [1]: ●, this work; ▲, ref. 5.

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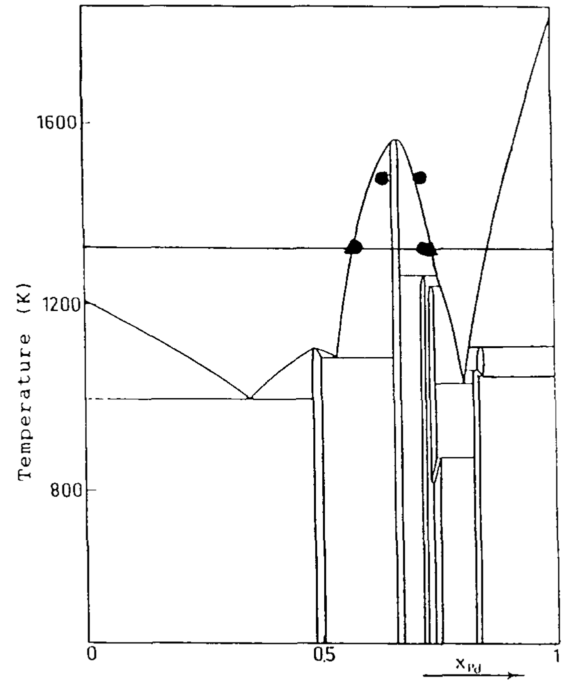

Fig. 2. Phase diagram of the Pd–Ge system according to Khalaff and Schubert [2]: ●, this work; ▲, ref. 5.

From the analysis of the thermodynamic behaviour of the melts according to the associated model [7, 8] we attributed their chemical short-range order to tendencies to form Pd_2Ge and PtGe associations respectively in agreement with the higher congruently melting compounds of the systems.

However, our previous calorimetric measurements were performed at two temperatures for Pt–Ge (1273 and 1352 K) whereas we measured the enthalpy of formation of Pd–Ge at only one temperature (1273 K). The purpose of this work was to measure the enthalpies of mixing of both liquid binaries in a temperature range large enough to determine their temperature dependence.

5. Calorimetric method

The apparatus employed were high temperature Calvet calorimeters built in the laboratory for $T < 1400$ K and purchased from Setaram for $1400 < T < 1800$ K. The drop method used (direct reaction calorimetry) has already been described [9]. The enthalpy of formation, ΔH_f, was deduced from the heat effects corresponding to successive additions of small quantities of platinum or palladium (from about 20 to 200 mg according to the concentration range) at T_0 (near 298 K) to a Pt_xGe_{1-x} or Pd_xGe_{1-x} binary alloy placed in an alumina crucible at the bottom of the calorimetric cell at temperature T. Before the first addition of platinum or palladium the melts were pure germanium (about 800 mg). At high temperature pure solid platinum or palladium was placed in the calorimetric cell at T instead of germanium and the mixing process was due to additions of germanium at T_0 in order to avoid losses of germanium by evaporation during the time necessary to reach thermal equilibrium.

At low temperatures ($T < 1400$ K) the thermal effects correspond in the case of Pt–Ge to the reaction

$$n\text{Pt}(\text{c}, 298\ \text{K}) + m\text{Pt}_x\text{Ge}_{1-x}(\text{l}, T) \longrightarrow (n+m)\text{Pt}_{x+dx}\text{Ge}_{1-x-dx}(\text{l}, T)$$

They lead to the integral enthalpy of formation of the melt with respect to composition.

The pure metals used were purchased from Koch–Light with metallic impurities less than 10^{-3} mass%. The calibration of the calorimeter was performed by adding small quantities of pure Ge(c, 298 K) into pure Ge(l, T). The enthalpy changes of platinum, palladium and germanium were taken from ref. 10. The calibration data were controlled by adding some small pieces of α-alumina (US National Bureau of Standards), the enthalpy change of which from T_0 to T is well known [11].

The enthalpies of formation of Pt–Ge and Pd–Ge alloys were determined at three temperatures: 1279, 1473 and 1673 K for Pt–Ge and 1269, 1473 and 1683 K for Pd–Ge. The breaks of the integral enthalpy of mixing with respect to composition allowed us to determine some liquidus mole fractions.

3. Results

3.1. Pt–Ge system

Figures 3–5 show the molar integral enthalpy of formation of the melt at the three temperatures in-

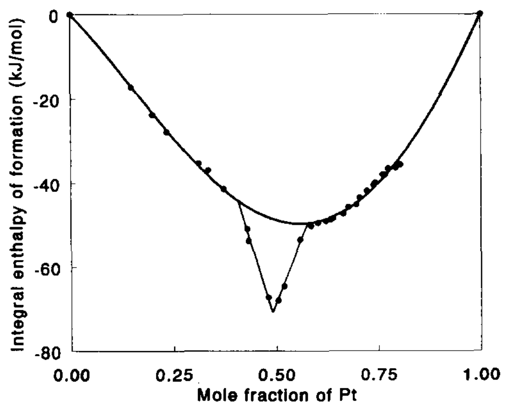

Fig. 3. Molar integral enthalpy of formation of the Pt–Ge alloys at 1279 K (this work) referred to both liquid components.

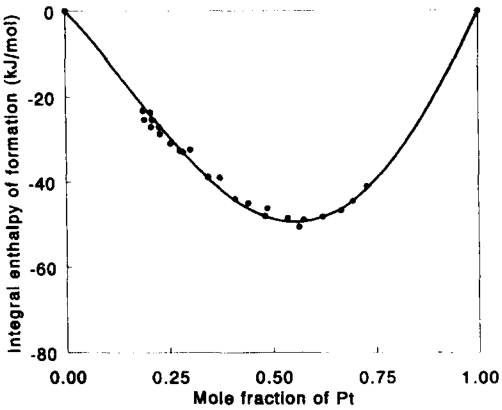

Fig. 4. Molar integral enthalpy of formation of the Pt–Ge alloys at 1473 K (this work) referred to both liquid components.

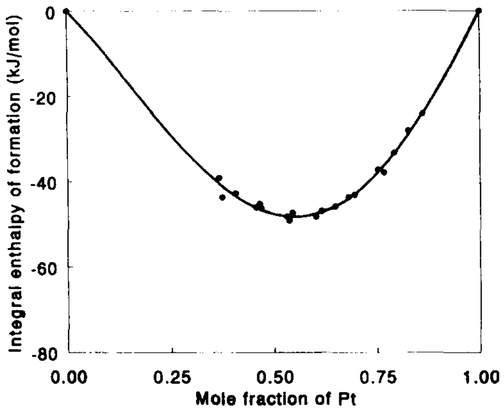

Fig. 5. Molar integral enthalpy of formation of the Pt–Ge alloys at 1673 K (this work) referred to both liquid components.

TABLE 1. Molar integral enthalpies of formation, ΔH_f, of the Pt–Ge alloys at 1279 K referred to both pure liquid components with respect to the platinum mole fraction x_{Pt} (experimental results)

x_{Pt}	ΔH^f (kJ mol^{-1})	x_{Pt}	ΔH^f (kJ mol^{-1})
0.199	−23.710	0.433	−53.812
0.334	−36.913	0.480	−67.201
0.430	−50.961	0.519	−64.559
0.504	−67.915	0.559	−53.506
0.593	−60.114	0.586	−50.273
0.633	−48.770	0.603	−49.543
0.664	−47.436	0.622	−49.057
0.696	−45.169	0.639	−48.490
0.738	−40.476	0.676	−45.755
0.767	−38.107	0.704	−43.448
		0.722	−41.860
0.149	−17.158	0.742	−39.894
0.234	−27.782	0.761	−38.004
0.311	−35.268	0.774	−36.558
0.372	−41.385		

vestigated with reference to the pure liquid components. The corresponding data given in Tables 1–4 lead to the following equations for the single liquid phase:

TABLE 2. Molar integral enthalpies of formation, ΔH_f, of the Pt–Ge alloys at 1473 K referred to both pure liquid components with respect to the platinum mole fraction x_{Pt} (experimental results)

x_{Pt}	ΔH^f (kJ mol^{-1})	x_{Pt}	ΔH^f (kJ mol^{-1})
0.191	−25.251	0.118	−14.771
0.207	−27.012	0.206	−23.583
0.228	−28.702	0.301	−32.409
0.253	−30.972	0.373	−37.451
0.276	−32.747	0.441	−41.832
0.345	−38.918	0.487	−44.231
0.481	−48.016	0.536	−47.389
		0.575	−48.288
0.188	−23.145	0.621	−48.222
0.210	−25.253	0.665	−46.658
0.227	−27.048	0.694	−44.456
0.283	−32.963	0.729	−41.000
0.344	−38.870	0.754	−35.803
0.409	−43.994		
0.564	−50.623		

TABLE 3. Molar integral enthalpies of formation, ΔH_f, of the Pt–Ge alloys at 1673 K referred to both pure liquid components with respect to the platinum mole fraction x_{Pt} (experimental results)

x_{Pt}	ΔH^f (kJ mol^{-1})	x_{Pt}	ΔH^f (kJ mol^{-1})
0.298	−37.259	0.468	−46.220
0.344	−40.374	0.530	−48.202
0.396	−43.528	0.601	−48.281
0.455	−46.041	0.695	−43.058
0.537	−48.519	0.827	−26.253
0.648	−45.777		
0.792	−31.902	0.464	−45.198
		0.544	−47.335
0.289	−38.471	0.615	−46.915
0.373	−43.634	0.680	−43.586
0.536	−49.140	0.752	−37.148
0.767	−37.865	0.861	−24.031
0.366	−39.048		
0.406	−42.716		

$$\Delta H_f\ (\text{kJ mol}^{-1}) = x_{Pt}(1-x_{Pt})(-107.42-193.37x_{Pt} -26.79x_{Pt}^2+127.93x_{Pt}^3 \quad \text{at 1279 K}$$

$$\Delta H_f\ (\text{kJ mol}^{-1}) = x_{Pt}(1-x_{Pt})(-95.34-287.65x_{Pt} +178.97x_{Pt}^2) \quad \text{at 1473 K}$$

$$\Delta H_f\ (\text{kJ mol}^{-1}) = x_{Pt}(1-x_{Pt})(-95.42-283.60x_{Pt} +187.14x_{Pt}^2) \quad \text{at 1673 K}$$

As can be seen in Fig. 6, the results agree well with the previous ones [6]. At 1279 K the breaks at $x_{Pt}=0.41$ and 0.58 correspond to the two (liquid–liquid + solid PtGe compound) boundaries. As shown in Fig. 1, they are close to the experimental data of the literature.

TABLE 4. Molar integral enthalpies of formation ΔH_f, of the Pt–Ge liquid alloys at the three temperatures investigated referred to both pure liquid components with respect to the platinum mole fraction x_{Pt} (smoothed values). Values on the platinum-rich side have been extrapolated and correspond to undercooled melts

x_{Pt}	ΔH^f (kJ mol^{-1})		
	1279 K	1473 K	1673 K
0.05	−5.58	−5.22	−5.19
0.10	−11.46	−11.04	−10.98
0.15	−17.47	−17.17	−17.06
0.20	−23.45	−23.34	−23.15
0.25	−29.22	−29.29	−28.99
0.30	−34.62	−34.79	−34.37
0.35	−39.44	−39.63	−39.06
0.40	−43.53	−43.65	−42.94
0.45	−46.72	−46.69	−45.82
0.50	−48.86	−48.63	−47.61
0.55	−49.82	−49.37	−48.21
0.60	−49.50	−48.86	−47.57
0.65	−47.82	−47.04	−45.65
0.70	−44.74	−43.90	−42.46
0.75	−40.27	−39.45	−38.03
0.80	−34.45	−33.75	−32.40
0.85	−27.37	−26.84	−25.65
0.90	−19.18	−18.82	−17.90
0.95	−10.07	−9.82	−9.29

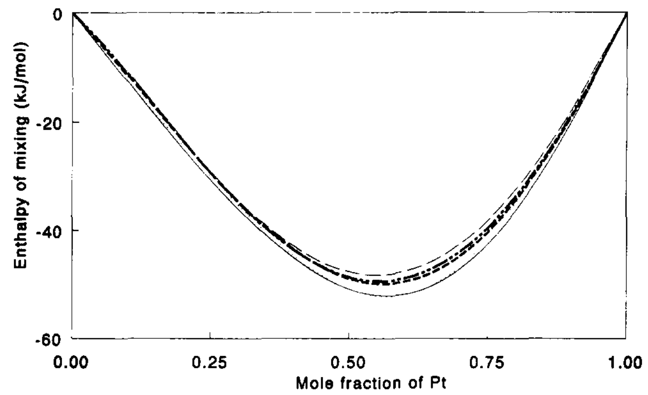

Fig. 6. Molar integral enthalpy of formation of the PtGe melts at the three temperatures investigated. The values corresponding to the solid–liquid domains are interpolated and those corresponding to the platinum-rich side are extrapolated: – – –, this work, 1279 K; - - - -, this work, 1473 K; ——, this work, 1673 K; · · · · ·, ref. 5, 1273 K; —, ref. 5, 1352 K.

At any investigated temperature the integral enthalpy of mixing is negative in the whole range of concentration and increases slowly when the temperature increases. The location of the minimum ($x_{Pt}=0.565$ at 1279 K, 0.558 at 1473 K and 0.551 at 1673 K) is slightly shifted towards the germanium-rich side with increasing temperature, *i.e.* towards the PtGe stoichiometry.

3.2. Pd–Ge system

The molar integral enthalpies of formation of the Pd–Ge melts at the three temperatures investigated are shown in Figs. 7–9 with reference to the pure liquid components. The corresponding data given in Tables 5–8 lead to the following equations for the single liquid phase:

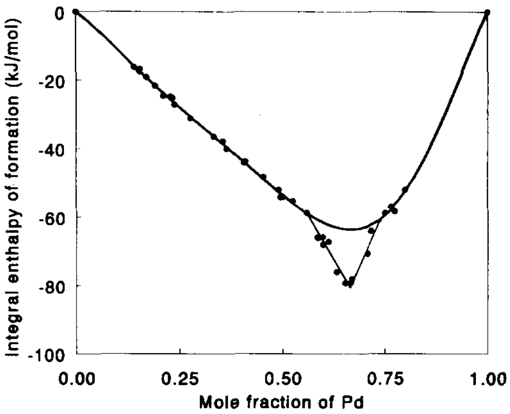

Fig. 7. Molar integral enthalpy of formation of the Pd–Ge alloys at 1269 K (this work) referred to both liquid components.

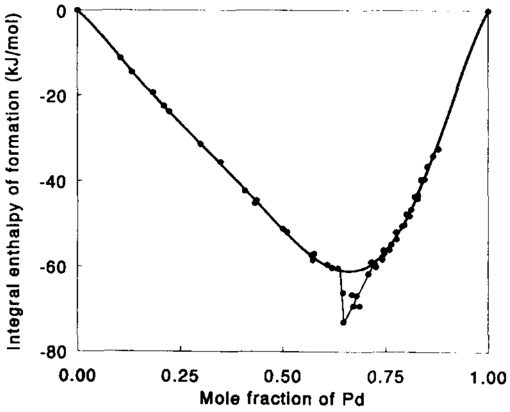

Fig. 8. Molar integral enthalpy of formation of the Pd–Ge alloys at 1473 K (this work) referred to both liquid components.

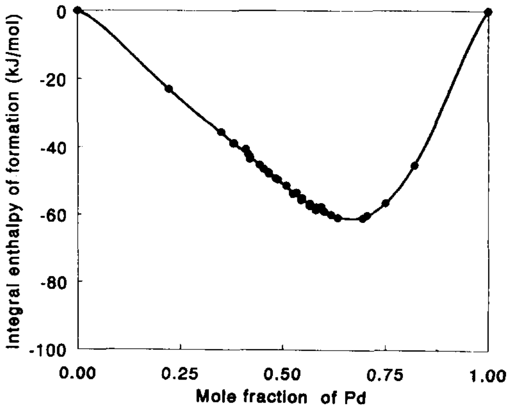

Fig. 9. Molar integral enthalpy of formation of the Pd–Ge alloys at 1683 K (this work) referred to both liquid components.

TABLE 5. Molar integral enthalpies of formation, ΔH_f, of the Pd–Ge alloys at 1269 K referred to both pure liquid components with respect to the palladium mole fraction x_{Pd} (experimental results)

x_{Pd}	ΔH^f (kJ mol^{-1})	x_{Pd}	ΔH^f (kJ mol^{-1})
0.156	−16.750	0.715	−63.990
0.233	−25.130	0.742	−56.340
0.355	−37.860	0.750	−59.856
0.409	−43.692		
0.454	−48.273	0.142	−16.172
0.491	−52.064	0.154	−17.490
0.526	−55.373	0.170	−19.096
0.559	−58.726	0.191	−21.635
0.585	−65.932	0.211	−24.560
0.612	−67.170	0.238	−27.140
0.632	−75.980	0.277	−31.162
0.653	−79.482	0.333	−36.560
0.667	−79.065	0.406	−44.013
		0.501	−54.170
0.228	−24.790	0.599	−68.032
0.364	−40.720	0.669	−77.950
0.496	−54.212	0.766	−57.100
0.588	−65.965	0.800	−52.001
0.670	−72.396		

TABLE 6. Molar integral enthalpies of formation, ΔH_f, of the Pd–Ge alloys at 1473 K referred to both pure liquid components with respect to the palladium mole fraction x_{Pd} (experimental results)

x_{Pd}	ΔH^f (kJ mol^{-1})	x_{Pd}	ΔH^f (kJ mol^{-1})
0.106	−11.242	0.853	−36.607
0.212	−22.489	0.867	−34.075
0.349	−35.579	0.880	−32.416
0.436	−44.544		
0.511	−51.903	0.133	−14.87
0.577	−57.011	0.223	−23.795
0.635	−62.108	0.432	−45.143
0.680	−66.918	0.574	−58.448
0.715	−58.850	0.609	−59.520
0.745	−56.108	0.648	−73.090
0.776	−51.855	0.672	−69.369
0.801	−47.673	0.724	−59.326
0.822	−43.650	0.747	−56.948
0.838	−39.671	0.764	−54.800
0.847	−39.602	0.791	−50.468
		0.813	−46.602
0.184	−19.363	0.687	−69.366
0.300	−31.343	0.708	−61.682
0.409	−42.296	0.727	−60.108
0.501	−51.162	0.743	−58.295
0.571	−57.305	0.760	−56.004
0.621	−61.305	0.777	−53.485
0.647	−66.180	0.797	−50.205
0.669	−69.683	0.809	−48.130

TABLE 7. Molar integral enthalpies of formation, ΔH_f, of the Pd–Ge alloys at 1683 K referred to both pure liquid components with respect to the palladium mole fraction x_{Pd} (experimental results)

x_{Pd}	ΔH^f (kJ mol^{-1})	x_{Pd}	ΔH^f (kJ mol^{-1})
0.378	−38.813	0.380	−38.658
0.419	−42.801	0.415	−42.038
0.465	−47.446	0.443	−45.184
0.534	−53.448	0.466	−47.866
0.594	−57.623	0.488	−49.595
0.693	−54.124	0.509	−51.404
0.763	−41.594	0.532	−53.501
		0.548	−55.163
0.419	−43.453	0.567	−56.691
0.453	−46.384	0.583	−57.764
0.483	−49.226	0.601	−58.930
0.525	−53.882	0.618	−59.949
0.545	−55.635	0.634	−60.790
0.566	−57.309	0.652	−61.955
0.581	−58.522	0.668	−62.049
		0.682	−61.879
0.322	−32.866	0.694	−60.907
0.349	−35.496	0.705	−60.059

TABLE 8. Molar integral enthalpies of formation, ΔH_f, of the Pd–Ge liquid alloys at the three temperatures investigated referred to both pure liquid components with respect to the palladium mole fraction x_{Pd} (smoothed values). Values on the palladium rich side have been extrapolated and correspond to undercooled melts

x_{Pd}	ΔH^f (kJ mol^{-1})		
	1279 K	1473 K	1683 K
0.05	−4.91	−4.45	−3.43
0.10	−10.83	−10.15	−8.83
0.15	−16.80	−15.97	−14.74
0.20	−22.50	−21.43	−20.46
0.25	−27.85	−26.48	−25.79
0.30	−32.99	−31.28	−30.81
0.35	−38.08	−36.06	−35.74
0.40	−43.22	−40.99	−40.74
0.45	−48.41	−46.08	−45.84
0.50	−53.46	−51.13	−50.87
0.55	−58.00	−55.75	−55.48
0.60	−61.51	−59.32	−59.07
0.65	−63.35	−61.12	−60.93
0.70	−62.84	−60.40	−60.31
0.75	−59.37	−56.50	−56.56
0.80	−52.51	−49.08	−49.27
0.85	−42.22	−38.27	−38.57
0.90	−29.01	−24.96	−25.29
0.95	−14.17	−11.10	−11.35

$$\Delta H_f\ (\text{kJ mol}^{-1}) = x_{Pd}(1-x_{Pd})(-78.99-586.36x_{Pd} + 2156.8x_{Pd}^2-4347.5x_{Pd}^3 + 2601.2x_{Pd}^4) \quad \text{at } 1269\text{ K}$$

$$\Delta H_f\ (\text{kJ mol}^{-1}) = x_{Pd}(1-x_{Pd})(-64.06-714.22x_{Pd} + 2798.5x_{Pd}^2-5542.7x_{Pd}^3 + 3358.3x_{Pd}^4) \quad \text{at } 1473\text{K}$$

$$\Delta H_f\ (\text{kJ mol}^{-1}) = x_{Pd}(1-x_{Pd})(-33.99-913.14x_{Pd} + 3285.2x_{Pd}^2-6039.0x_{Pd}^3 \quad \text{27,,,R,I0} \quad + 3530.2x_{Pd}^4) \quad \text{at } 1683\text{ K}$$

At 1269 and 1473 K the breaks at $x_{Pd}=0.570$ and 0.731 and $x_{Pd}=0.636$ and 0.715 respectively correspond to the two (liquid–liquid + solid Pd_2Ge compound) boundaries. As shown in Fig. 2, they agree well with the literature data.

As shown on Fig. 10, the integral enthalpy of mixing is negative in the whole range of concentration at any investigated temperature and the new data are in agreement with the previous ones [6]. It increases with temperature and the location of the minimum ($x_{Pd}=0.666$ at 1269 K as well as at 1473 and 1673 K) is temperature independent.

3.3. PtGe and Pd_2Ge solid phases

Using the excess Gibbs free energy of mixing at 2053 K for Pt–Ge and at 1820 K for Pd–Ge measured in a previous work [6], *i.e.*

$$\Delta G^E\ (\text{kJ mol}^{-1}) = x_{Pt}(1-x_{Pt})(-88.11+141.34x_{Pt}-766.53x_{Pt}^2 + 629.56x_{Pt}^3) \quad \text{at } 2053\text{ K}$$

$$\Delta G^E\ (\text{kJ mol}^{-1}) = x_{Pd}(1-x_{Pd})(-91.49+67.12x_{Pd}-795.04x_{Pd}^2 + 671.11x_{Pd}^3) \quad \text{at } 1820\text{ K}$$

and the values of the enthalpies of formation of the PtGe and Pd_2Ge solid compounds determined in this work, *i.e.* ΔH_f (kJ mol^{-1} of atoms) = −71.61 for PtGe and −75.49 for Pd_2Ge, we calculated the excess entropies of formation of these intermediate phases at their melting temperatures as ΔS_f^E (kJ K^{-1} mol^{-1} of atoms) = −0.025 for PtGe and −0.021 for Pd_2Ge. These lead to the following expressions for the Gibbs enthalpies of formation of the solid compounds:

$$\Delta G_f(\text{PtGe})\ (\text{kJ mol}^{-1}) = -71.61-5.738T$$

$$\Delta G_f(\text{Pd}_2\text{Ge})\ (\text{kJ mol}^{-1}) = -75.49-5.271T$$

The liquid–solid compound boundaries calculated in this way, assuming no temperature dependence of the enthalpy of formation of the compounds, are shown in Figs. 11 and 12. For Pd–Ge the calculated liquidus is in good agreement with the experimental determinations of Khalaff and Schubert [2] and with our new (this work, 1269 and 1473 K) and previous (ref. 5, 1270 K) experimental data derived from the breaks of $\Delta H_f(x)$. For Pt–Ge our calculations agree well with the phase boundaries determined by Oya and Suzuki [1] but not with the older ones of Jain and Bhan [4]. Our previous experimental results at 1275 K and the new ones at 1279 K agree also with Oya and Suzuki but not with Jain and Bhan.

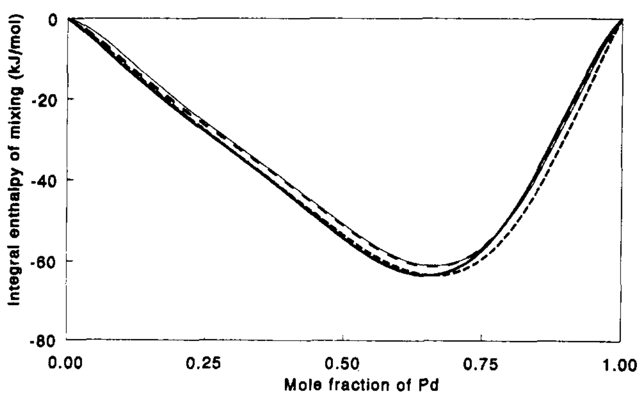

Fig. 10. Molar integral enthalpy of formation of the Pd–Ge melts at the three temperatures investigated. The values corresponding to the solid–liquid domains are interpolated and those corresponding to the palladium-rich side are extrapolated: – – –, this work, 1269 K; — —, this work, 1473 K; ——, this work, 1683 K; ——, ref. 5, 1270 K.

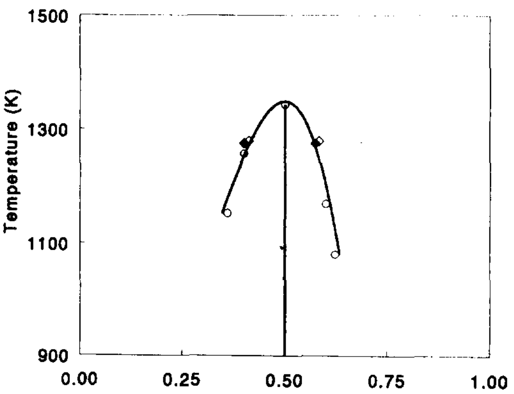

Fig. 11. PtGe–liquid phase boundaries. The open circles correspond to the phase diagram of Oya and Suzuki [1] and the solid line corresponds to the equilibrium phase diagram calculated as indicated in the text; ◇ and ◆ are deduced from the breaks of the ΔH_f curves (respectively ref. 5 and this work).

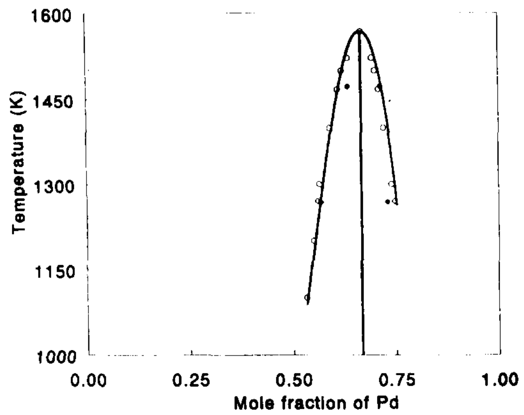

Fig. 12. Pd_2Ge–liquid phase boundaries. The open circles correspond to the phase diagram of Khalaff and Schubert [2] and the solid line corresponds to the equilibrium phase diagram calculated as indicated in the text; ◇ and ◆ are deduced from the breaks of the ΔH_f curves (respectively ref. 5 and this work).

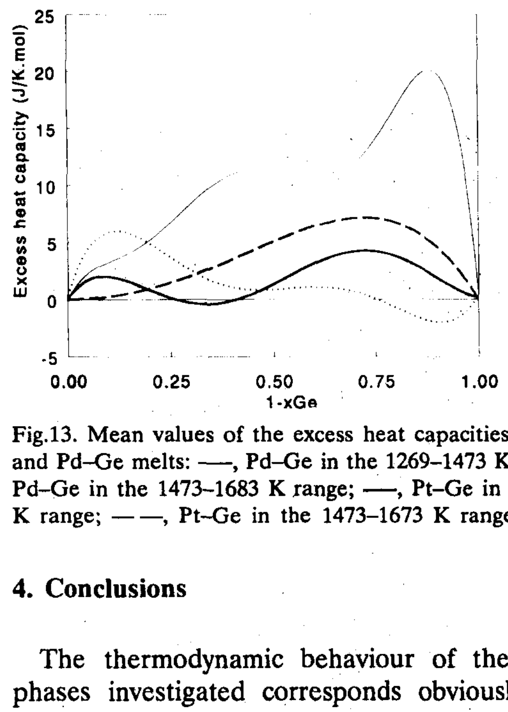

Fig.13. Mean values of the excess heat capacities of the Pt–Ge and Pd–Ge melts: ——, Pd–Ge in the 1269–1473 K range; · · · · ·, Pd–Ge in the 1473–1683 K range; ——, Pt–Ge in the 1279–1473 K range; — — —, Pt–Ge in the 1473–1673 K range.

4. Conclusions

The thermodynamic behaviour of the two liquid phases investigated corresponds obviously to strong short-range order, since their enthalpies of formation are strongly negative in the whole range of concentration. Moreover, the thermal stability of the associates is high, since the excess heat capacities are very low (Fig. 13).

The minimum of the enthalpy of mixing of the Pt–Ge melts lies between Pt_2Ge and PtGe. The experimental shift towards the germanium-rich side with increasing temperature agrees well with the higher melting point of PtGe than that of Pt_2Ge (the PtGe associates are less destroyed by thermal agitation). In contrast, the minimum of the enthalpy of formation of the Pd–Ge liquid phase corresponds to the Pd_2Ge stoichiometry at any temperature, in agreement with the large difference between the melting points of the two congruently melting compounds. Moreover, the temperature of fusion of Pd_2Ge is very much higher than that of PtGe. Such conclusions agree well with the differences between the experimental values of the entropies of melting and those calculated by additivity:

$$\delta\Delta S^{\text{fus}} = \Delta S^{\text{fus}}\,(\text{exp}) - \sum_i x_i \Delta S_i^{\text{fus}}$$

where ΔS_i^{fus} is the entropy of melting of the pure component i. Indeed, the corresponding values of $\delta\Delta S^{\text{fus}}$ (-2.29 for PtGe and -4.99 for Pd_2Ge) lead to the conclusion that the PtGe and Pd_2Ge clusters are only weakly destroyed upon melting and that the stability of Pd_2Ge is higher than that of PtGe.

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