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Letter

Calorimetric determination of the enthalpies of formation of the solid compounds of the Pt–Ge system

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Abstract

The enthalpies of formation of the solid intermediate compounds of the Pt–Ge system were determined at 298 K by direct reaction calorimetry (drop method) using a high-temperature Calvet calorimeter. The selected data are: h^f/kJ mol^{-1} = -32.4 ± 0.8 ($Pt_{0.333}Ge_{0.667}$); -41.9 ± 2.7 ($Pt_{0.4}Ge_{0.6}$); -45.0 ± 1.5 ($Pt_{0.5}Ge_{0.5}$); -42.4 ± 0.7 ($Pt_{0.6}Ge_{0.4}$); -37.3 ± 0.5 ($Pt_{0.667}Ge_{0.333}$); -32.5 ± 2.6 ($Pt_{0.75}Ge_{0.25}$).

1. Introduction

According to Oya and Suzuki [1] there are six intermediate compounds in the Pt–Ge binary system: Ge_2Pt, Ge_3Pt_2, GePt, Ge_2Pt_3, $GePt_2$ and $GePt_3$. Thermodynamic data concerning these solid phases are very scarce as we know only the enthalpy of formation of PtGe and Pt_2Ge. Concerning $Pt_{0.5}Ge_{0.5}$, our previous data [2, 3] obtained by adding successively at high temperature small quantities of solid Pt to liquid Ge up to the point of formation of the intermediate phase led to the following values: −46.3 kJ mol^{-1} at 1273 K and −43.3 kJ mol^{-1} at 1279 K. They agree well with that of Kleppa [4] determined in the same way as used here (−45.4 kJ mol^{-1} at 298 K). For $Pt_{0.667}Ge_{0.333}$, Kleppa [4] found −37.1 kJ mol^{-1}. To our knowledge there are no data concerning the other solid phases. The purpose of this work, therefore, was to determine the enthalpy of formation of the last five compounds.

2. Calorimetric method

The apparatus employed was a high-temperature (T/K < 1400) Calvet calorimeter built in the laboratory. The drop method used here (direct reaction calorimetry again) is somewhat different from that used previously.

In the first investigation [5] we added successively small quantities of solid Pt(298 K) to the liquid alloy (pure liquid Ge at temperature T_c before the first addition of Pt) up to obtain the composition of the compound. In such a way we obtained the enthalpy of formation at the temperature T_c of the calorimeter *i.e.* at high temperature.

With the method used here, as a first step we dropped into the calorimetric cell a mechanical mixture of solid Pt and Ge (100–200 mg) corresponding to the stoichiometry of the intermediate phase. In most cases, T_c is above the melting point of Ge (1210 K). Then Ge melts and dissolves Pt to give the alloy

$$\mathrm{aPt(cr}, T_0) + \mathrm{bGe(cr}, T_0) \longrightarrow \mathrm{Pt}_x\mathrm{Ge}_{1-x}(T_c) \qquad h_1 \quad (1)$$

When T_c is above the liquidus temperature, the final state corresponds to a single liquid phase. When T_c is below the liquidus but above the peritectic temperature, the final state is a solid–liquid two-phase alloy. Moreover, in some cases (see Table 1) T_c is just below the melting point of Ge and the reaction takes place between solid Ge and solid Pt to give the equilibrium state as verified by X-ray measurements.

TABLE 1. Experimental data corresponding to the temperatures T_c of reaction (1), to the enthalpy terms h_1 and h_2 of the reactions (1) and (2) respectively and to the enthalpies of formation of the compounds referred to pure solid components per mole of compound

Compound	T_c (K)	H_1 (kJ mol^{-1})	h_2 (kJ mol^{-1})	h^f (298 K) (kJ mol^{-1})
$PtGe_2$	1317	68.13	169.07	−100.94
	1230	55.41	152.06	−96.65
	1226	55.40	150.93	−95.53
	1164[a]	52.42	148.52	−96.10
Pt_2Ge_3	1328	79.12	304.41	−225.29
	1263	72.86	275.23	−202.37
	1226	46.62	201.58	−201.58
Pt_3Ge_2	1383	33.95	242.16	−208.21
	1379	25.94	239.93	−213.99
	1263	15.96	230.43	−214.47
Pt_2Ge	1164[a]	1.24	113.28	−112.04
	1164[a]	1.23	112.75	−111.52
Pt_3Ge	1317	43.69	176.56	−132.87
	1230	23.65	161.87	−138.22
	1226	23.65	142.11	−118.46

[a] Reaction (1) took place at a temperature below the melting point of pure Ge.

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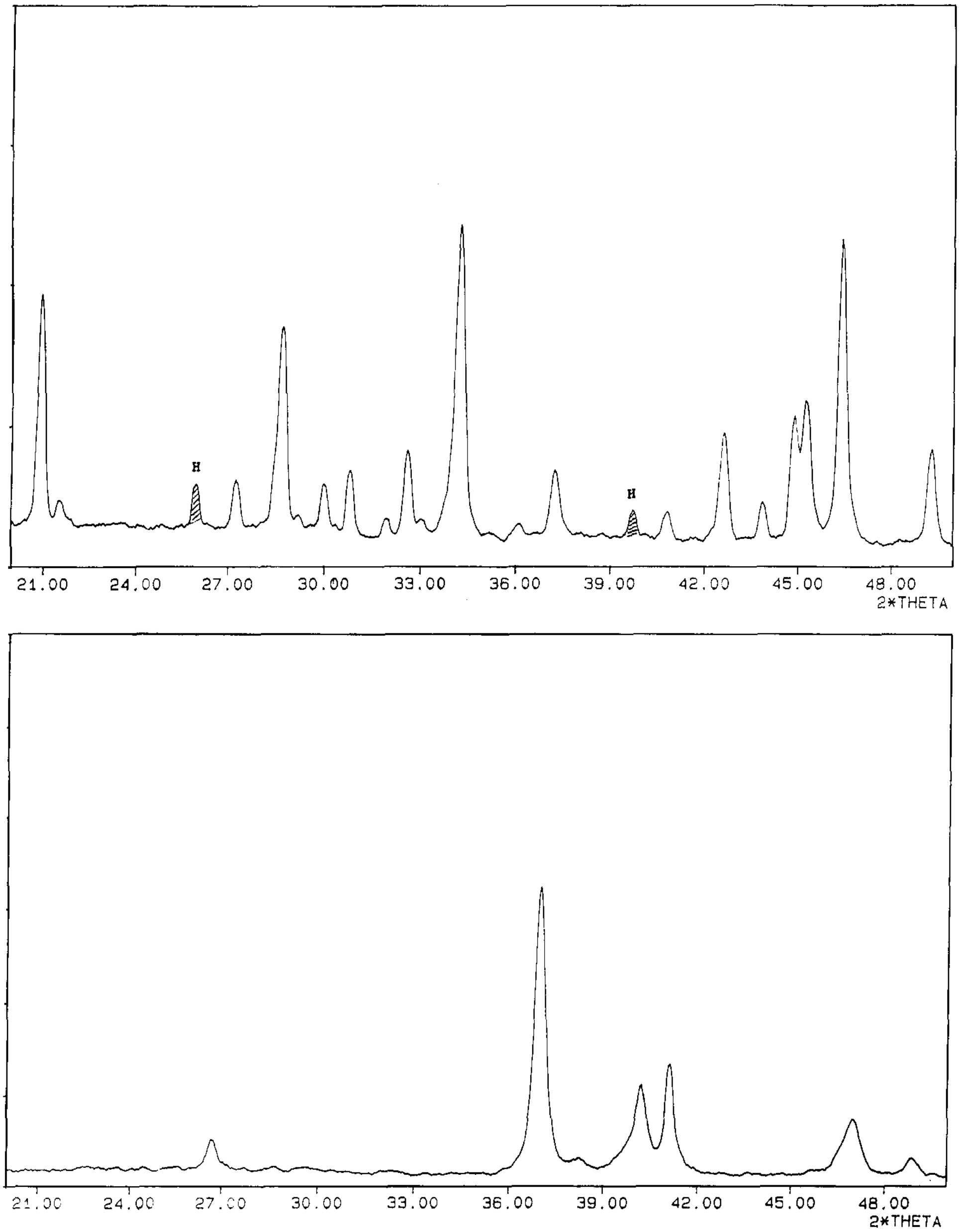

Fig. 1. X-ray diffraction obtained with the Kαl ray of copper ($\lambda = 1.54$ Å, $U = 40$ kV, $I = 25$ mA and $t = 1197$ s) on Ge_2Pe (upper part) and $GePt_2$ (lower part) samples prepared at 1230 K and 1164 K respectively by direct reaction between pure solid Pt and Ge and annealed at 973 K for about 24 h. In the case of $GePt_2$ all the rays observed correspond to the solid compound. For Ge_2Pt, two extra rays corresponding to Ge_3Pt_2 are shown by shaded areas and marked H.

After annealing for 24 h at about 150 K below the peritectic temperature in order to be sure of good crystallization, we cooled the alloy slowly at room temperature. We then measured in a second step the variation of the heat content of the alloy between T_0 (near 298 K) and T_c:

$$Pt_aGe_b(cr, T_0) \longrightarrow Pt_xGe_{1-x}(T_c) \qquad h_2 \qquad (2)$$

Since the final state of reactions (1) and (2) are the same, we deduced the enthalpy of formation h^f of the solid alloy at T_0:

$$aPt(cr, T_0) + bGe(cr, T_0) \longrightarrow Pt_aGe_b(cr, T_0) \qquad (3)$$

$$h^f = h_1 - h_2$$

The pure metals used were purchased from Koch-Light; they had metallic impurities of less than 10^{-3} mass%. The calibration of the calorimeter was performed by adding some small pieces of α-alumina (US National Bureau of Standards), the enthalpy change of which (from T_0 to T_c) is well known [6].

TABLE 2. Selected values of the enthalpies of formation of the solid PtGe compounds at 298 K per mole of metallic atoms with reference to pure solid components

Compound	h^f(kJ mol^{-1} of atoms)
$Pt_{0.333}Ge_{0.667}$	-32.4 ± 0.8
$Pt_{0.4}Ge_{0.6}$	-41.9 ± 2.7
$Pt_{0.5}Ge_{0.5}$	-45.0 ± 1.5
$Pt_{0.6}Ge_{0.4}$	-42.4 ± 0.7
$Pt_{0.667}Ge_{0.333}$	-37.3 ± 0.5
$Pt_{0.75}Ge_{0.25}$	-32.5 ± 2.6

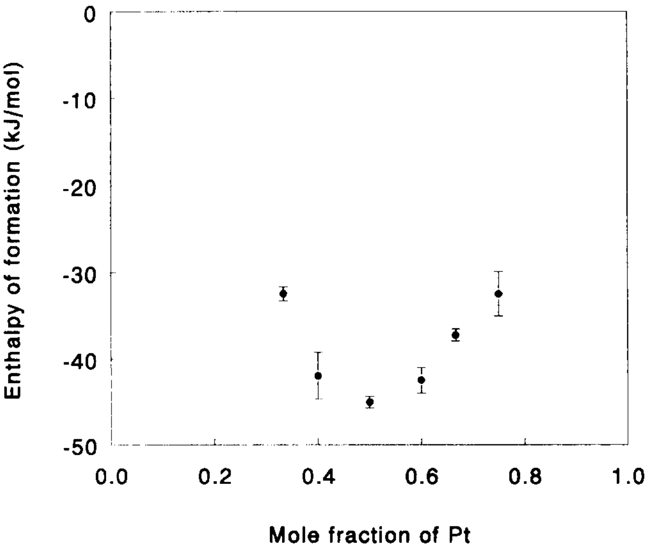

Fig. 2. Molar integral enthalpy of formation of the Pt–Ge solid alloys at 298 K referred to both solid components and to a mole of atoms.

3. Results and discussion

The structure of the solid samples after annealing were verified by X-ray measurements using the Kαl of Cu ($\lambda = 1.54$ Å, $U = 40$ kV, $I = 25$ mA and $t = 1197$ s). In the case of Pt_2Ge_3, Pt_3Ge_2 and $PtGe_2$, we observed some extra rays (marked H on Fig. 1) corresponding to neighbouring compounds, the proportions of which were estimated not to exceed 2 at.%. No correction was taken into account for such deviations to single phase. As an example, the X-ray diffractograms for Pt_2Ge and $PtGe_2$ are shown in the top and bottom parts respectively of Fig. 1.

The experimental data obtained for the five alloys investigated are given in Table 1, with reference to a mole of molecules. We deduced from them the mean values given in Table 2 referred to a mole of atoms.

Figure 2 shows the molar integral enthalpy of formation (at room temperature except for $Pt_{0.5}Ge_{0.5}$) of the Pt_xGe_{1-x} alloys with reference to pure solid components plotted against platinum mole fraction. As can be seen, the minimum of the enthalpy corresponds to PtGe *i.e.* the single congruently melting compound of the system. If we neglect the entropy term of the Gibbs free energy, the results suggest stable solid compounds at 298 K with respect to the neighbouring compounds, in agreement with the published phase diagram.

We will report in the future a critical assessment of the Pt–Ge binary system calculated from the data on the solid compounds obtained here and from the thermodynamic functions of the melt measured previously *i.e.* enthalpy [2, 3] and Gibbs free energy of mixing [7].

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