Thermodynamics of the (Pt + Ga) system

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Abstract

The integral enthalpy of mixing ($\Delta_{mix}H_m^\circ = f(x_{Pt})$) of the (Pt + Ga) liquid system was measured using a very high temperature calorimeter in the temperature and molar fraction ranges $1071 < T/K < 1465$ and $0 < x_{Pt} < 0.61$ respectively. It can be described by the following equation: $\Delta_{mix}H_m^\circ = x_{Pt}(1 - x_{Pt}) \cdot \xi(x_{Pt})$ kJ mol^{-1}, with $\xi(x_{Pt}) = -150.19 - 308.28x_{Pt} + 126.28x_{Pt}^2 + 131.88x_{Pt}^3 - 14.31x_{Pt}^4$. This function is negative with a minimum $\Delta_{mix}H_m^\circ = -64.5 \pm 2$ kJ mol^{-1} at $x_{Pt} = 0.52 \pm 0.01$, and is independent of temperature within experimental error. The limiting partial molar enthalpy of supercooled liquid platinum in liquid gallium, deduced from experiments performed between 1169 K and 1180 K, is $\Delta_{mix}h_m^\circ$ (Pt supercooled liq in ∞ liq Ga) = -151 ± 5 kJ mol^{-1}. However, by extrapolation of the ξ-function to $x_{Pt} = 1$, the limiting enthalpy of Ga in supercooled liquid Pt was obtained: $\Delta_{mix}h_m^\circ$(Ga liq in ∞ supercooled liq Pt) = -215 ± 30 kJ mol^{-1}. Moreover, from calorimetric measurements performed at 1350 K, the enthalpies of formation and of fusion of the PtGa definite compound were determined: $\Delta_{for}H_m^\circ$(PtGa) = -69.5 kJ mol^{-1}, $\Delta_{fus}H_m^\circ$(PtGa) = $+5.1$ kJ mol^{-1}. In addition, some points of the liquidus were deduced: $x_{Pt} = 0.15_8$ with $T = 1071$ K; $x_{Pt} = 0.21_3$ with $T = 1125$ K; $x_{Pt} = 0.25_1$ with $T = 1175$ K; $x_{Pt} = 0.54_5$ with $T = 1325$ K; $x_{Pt} = 0.42_5$ and $x_{Pt} = 0.53_5$ with $T = 1350$ K then $x_{Pt} = 0.47_0$ and $x_{Pt} = 0.52_5$ with $T = 1366$ K. For two compositions ($x_{Pt} = 0.5$ and $x_{Pt} = 0.62_5$), the molar heat capacities were measured between 423 and 763 K. The enthalpies of mixing were compared with the data (i) previously obtained with solid alloys, (ii) predicted by Miedema's empirical model, (iii) measured for the homologous systems (Pd + Ga), (Pd + In) and (Pt + In). The energetic effect is due to a transfer from Ga to Pt of 2.5 electrons at most in the highest Pt-band.

Keywords: Thermodynamics; Platinum–gallium alloy; Enthalpy of formation; Enthalpy of mixing; High temperature calorimetry; Liquid alloys

1. Introduction

In the past few years, much information has been accumulated on the thermodynamic properties of liquid binary alloys formed between a transition metal (nickel or palladium) and a polyvalent non-transition metal (aluminium, gallium or indium) [1–4]. These liquid systems are characterized by a high negative enthalpy of mixing, in both the solid and liquid states, caused by the overlap of d-type wave functions with p-type wave functions [5]. Now experimental investigations have been extended to the Pt-based systems: results on the (Pt + In) system have been published recently [6]; in this paper the enthalpies of formation of the (Pt + Ga) liquid alloy are presented.

2. Bibliographic review

2.1. Equilibrium phase diagram

The equilibrium phase diagram (Fig. 1), proposed by Guex and Feschotte [7] and redrawn by Massalski [8], seems reasonably well established and is used as reference for this work. This diagram exhibits several (eight) intermediate compounds; most of them (five) melt peritectically. These compounds are as follows (in this section, the temperatures are reported in degrees celsius instead of kelvin, in conformity with the phase diagram reprint of Massalski).

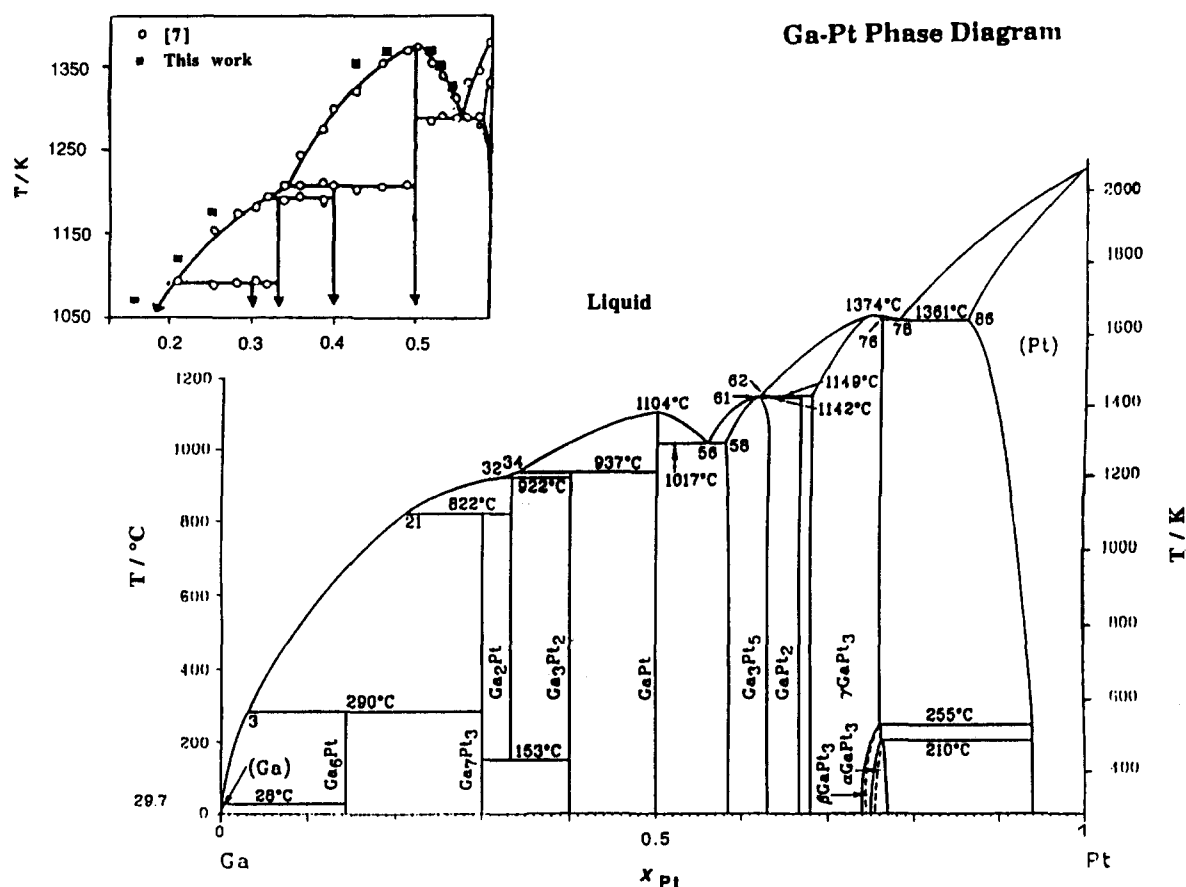*PtGa$_6$*. Orthorhombic, melts at 290 °C (PtGa$_6$ ↔ Liq + Pt$_3$Ga$_7$).

Fig. 1. Equilibrium phase diagram from Massalski [8].

Pt$_3$Ga$_7$. Centered cubic, melts at 822 °C (Pt$_3$Ga$_7$ ↔ Liq + PtGa$_2$).

PtGa$_2$. Face centered cubic, exists between 153 °C (Pt$_3$Ga$_7$ + Pt$_2$Ga$_3$ ↔ PtGa$_2$) and 922 °C (PtGa$_2$ ↔ Liq + Pt$_2$Ga$_3$).

Pt$_2$Ga$_3$. Hexagonal, is decomposed at 937 °C (PtGa$_3$ ↔ Liq + PtGa).

PtGa. Cubic, melts congruently at 1104 °C (PtGa ↔ Liq).

Pt$_5$Ga$_3$. Orthorhombic, has a range of non-stoichiometry (0.58 < x_{Pt} < 0.63) and melts congruently at 1142 °C (Pt$_5$Ga$_3$ ↔ Liq).

Pt$_2$Ga. Melts peritectically at 1149 °C (γ – Pt$_2$Ga ↔ Liq + γ – Pt$_3$Ga). This compound can present three structural forms: α – Pt$_2$Ga (tetragonal) below 605 °C, β – Pt$_2$Ga (orthorhombic) between 605 and 859 °C, and γ – Pt$_2$Ga (orthorhombic) between 605 and 1149 °C.

Pt$_3$Ga. Presents three structural forms: α – Pt$_3$Ga (tetragonal), with 0.75 < x_{Pt} < 0.77, decomposes at

210 °C (α – Pt$_3$Ga ↔ β – Pt$_3$Ga + (Pt)); β – Pt$_3$Ga (tetragonal), with 0.74 < x_{Pt} < 0.76, decomposes at 255 °C (β – Pt$_3$Ga ↔ γ – Pt$_3$Ga + (Pt)); γ-Pt$_3$Ga (cubic), with 0.67 < x_{Pt} < 0.76, can melt congruently at 1374 °C (γ – Pt$_3$Ga ↔ Liq). Moreover, the (Pt + Ga) system exhibits two eutectic points: at 1017 °C, Liq ↔ Pt$_5$Ga$_3$ + PtGa; at 1361 °C, Liq ↔ γ – Pt$_3$Ga + (solid solution 14 at.% Ga).

The solubility of solid gallium in solid platinum is relatively large with a maximum x_{Ga} = 0.14 at 1361 °C. The stoichiometric compounds, however, are found in the Ga-rich half of the equilibrium phase diagram, whereas in the other half all compounds show a significant range of non-stoichiometry.

2.2. Thermodynamic functions

Apart from the phase diagram, thermodynamic information is very scarce. Vogelbein et al. [9] measured the enthalpies of formation of Pt$_{75}$Ga$_{25}$ and Pt$_{94}$Ga$_6$ respectively by solution calorimetry in Pb and Sn liquid baths. Miedema and coworkers [5] calculated the enthalpy of mixing by modelization. Katayama et al. [10] performed emf measurements to obtain the gallium activity at 1100 K of the solid alloys only.

3. Experimental procedure

The enthalpies of formation of the liquid (Pt + Ga) system were measured with a very high temperature calorimeter using the direct drop method [11].

3.1. Calorimeter

Measurements at $1200 < T/K < 1500$ were performed using a very high temperature calorimeter (THT) of the Eyraud-Petit type described elsewhere [12,13], equipped with an automated sample charger. The calorimeter cell employed was an alumina tube closed at the lower end and shaped to fit into the thermopile. At first, before starting a series of measurements, the experimental graphite crucible was charged with a fixed amount of Ga (about 0.2–0.4 g) and introduced in the alumina tube. The calorimeter was then assembled and heated to the working temperature. Small pieces of Pt (between 20 and 60 mg) were added consecutively into the bath formed by pure gallium first, then by the liquid alloy. Measurements at $T = 1169$ K and $T = 1180$ K were taken using a Calvet calorimeter [14] with a quartz cell and a large experimental graphite crucible filled with about 4 g gallium. The procedure employed was identical with the procedure applied for the THT calorimeter. Between 423 and 763 K, the molar heat capacities of two alloys were obtained using a differential scanning calorimeter (DSC) [15].

3.2. Materials

High purity metals were employed in this study: 99.99 wt.% platinum (Degussa, FRG) and 99.999% wt.% gallium (Johnson Matthey). The platinum was cut into small pieces, rinsed with high purity acetone (pro analysis, Merck), and dried in air. The gallium was melted under a dilute solution of hydrochloric acid (5%) in warm water, divided into small droplets, and dried after rinsing with cold distilled water. A small flow of high purity argon (Argon N 56 from Air Liquide Company) is maintained during the measurements in the experimental chamber. Crucibles made of pure graphite (Carbone Lorraine Co.) were used as experimental cells to synthesize the alloys.

3.3. Calibration and precision

For each experiment, the calorimeter was calibrated at the end of each measurement series by dropping known amounts of α-alumina (purchased from NIST (National Institute of Standards and Technology, Washington, DC 20234)) from ambient temperature into the calorimeter at working temperature. The relative enthalpies of the α-alumina pieces were calculated by using the $C_p = f(T)$ data published by NIST. Relative enthalpies of platinum were taken from Barin and Knacke [16] assuming a constant value ($-34.727 \, \text{J K}^{-1} \, \text{mol}^{-1}$) for the heat capacity of the liquid and the supercooled liquid phase. In the experimental temperature range ($1200 < T/K < 1500$) the vapor pressures of platinum and gallium are sufficiently low to assume negligible loss of metal by evaporation. However, each alloy was weighed after the end of a measurement series and compared with the sum of the masses of the charged metals. The differences detected were less than 0.5% of the total mass. Heat transfer processes during dropping of the α-alumina and platinum samples were assumed as the main source of error. The error in the enthalpies of mixing was estimated to be of the same order of magnitude as the scatter (about 5%) found with the calibration drops of α-alumina. The experimental temperatures were obtained by a Pt–Rh6wt.%/Pt–Rh30wt.% thermocouple with an accuracy of ± 2 K, at least.

4. Results

Taking into account the shape of the phase diagram, experiments were performed from 1100 K to 1500 K to obtain the enthalpies of mixing over the entire stable concentration range of the liquid phase:

at 1071 K, $0 < x_{Pt} < 0.32_3$ at 1125 K, $0 < x_{Pt} < 0.33_8$

at 1175 K, $0 < x_{Pt} < 0.39_9$ at 1325 K, $0 < x_{Pt} < 0.59_3$

at 1350 K, $0 < x_{Pt} < 0.54_7$ at 1351 K, $0 < x_{Pt} < 0.60_9$

at 1353 K, $0 < x_{Pt} < 0.56_9$ at 1366 K, $0 < x_{Pt} < 0.56_4$

at 1406 K, $0 < x_{Pt} < 0.58_6$ at 1465 K, $0 < x_{Pt} < 0.54_0$

The experimental integral molar enthalpies (in kJ mol^{-1}) are gathered in Table 1. Values marked with an asterisk (*) correspond to the formation of a two-phase solid–liquid alloy.

4.1. Excess enthalpy in liquid Platinum + Gallium

4.1.1. Molar integral enthalpy

The experimental data presented in Fig. 2 reveal a very strong interaction in (Pt + Ga) alloys by the V-shaped $\Delta_{mix}H_m^\circ = f(x_{Pt})$ curve. The minimum is located at $x_{Pt} = 0.52$ with $\Delta_{mix}H_m^\circ = -64.5 \pm 2 \, \text{kJ mol}^{-1}$. The scatter between all the results is low (less than 4%). Taking into account the experimental uncertainty and the temperature range investigated, the enthalpy of formation of the liquid phase may be

Table 1
Experimental results ($\Delta_{mix}H_m^\circ = f(x_{Pt})$ kJ mol^{-1}) obtained by high temperature calorimetry

1071 K $m_{Ga} = 0.20997$ g		1125 K $m_{Ga} = 0.21640$ g		1175 K $m_{Ga} = 0.22068$ g ·		1325 K $m_{Ga} = 0.22196$ g		1350 K $m_{Ga} = 0.20732$ g	
x_{Pt}	$\Delta_{mix}H_m^\circ$	x_{Pt}	$\Delta_{mix}H_m^\circ$	x_{pt}	$\Delta_{mix}H_m^\circ$	x_{Pt}	$\Delta_{mix}H_m^\circ$	x_{Pt}	$\Delta_{mix}H_m^\circ$
0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
0.0379	-5.91	0.0294	-4.07	0.0417	-7.20	0.0469	-7.35	0.0384	-6.69
0.0717	-11.33	0.0633	-9.00	0.0733	-12.08	0.0909	-14.52	0.0756	-12.40
0.1048	-16.71	0.1047	-15.84	0.1157	-18.62	0.1326	-21.12	0.1102	-18.52
0.1397	-22.35	0.1547	-24.03	0.1653	-26.86	0.1721	-27.39	0.1431	-23.76
0.1749*	-25.80*	0.2066	-32.70	0.2085	-33.90	0.2088	-33.27	0.1749	-30.00
0.2083*	-25.73*	0.2545*	-34.32*	0.2549*	-40.79*	0.2434	-38.64	0.2050	-34.66
0.2488*	-25.59*	0.2984*	-33.39*	0.2699*	-40.56*	0.2759	-43.90	0.2332	-38.41
0.2879*	-25.44*	0.3376*	-32.89*	0.2976*	-39.93	0.3057	-47.99	0.2599	-43.07
0.3235*	-25.19*			0.3275*	-39.38*	0.3335	-51.66	0.2860	-46.64
				0.3566*	-38.97*	0.3592	-54.47	0.3106	-50.18
				0.3932*	-38.18*	0.3831	-57.04	0.3335	-53.46
						0.4055	-59.11	0.3551	-56.23
						0.4263*	-60.52*	0.3754	-58.35
						0.4465*	-62.01*	0.3949	-60.65
						0.4656*	-62.94*	0.4135	-62.07
						0.4838*	-63.56*	0.4311	-63.33
						0.5010*	-64.35*	0.4480*	-64.55*
						0.5173*	-64.75*	0.4641*	-65.59*
						0.5325*	-64.20*	0.4794*	-66.21*
						0.5470*	-60.57*	0.4963*	-67.24*
						0.5614*	-58.90*	0.5126*	-67.66*
						0.5775*	-57.75*	0.5301*	-65.63*
						0.5933*	-56.36*	0.5468*	-60.90*

1351 K $m_{Ga} = 0.20872$ g		1353 K $m_{Ga} = 0.21781$ g		1366 K $m_{Ga} = 0.22737$ g		1406 K $m_{Ga} = 0.22974$ g		1465 K $m_{Ga} = 0.23743$ g	
x_{Pt}	$\Delta_{mix}H_m^\circ$	x_{Pt}	$\Delta_{mix}H_m^\circ$	x_{pt}	$\Delta_{mix}H_m^\circ$	x_{Pt}	$\Delta_{mix}H_m^\circ$	x_{Pt}	$\Delta_{mix}H_m^\circ$
0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
0.0790	-12.83	0.0838	-12.80	0.0472	-7.67	0.04963	-7.80	0.0433	-7.98
0.1479	-24.31	0.1699	-27.31	0.0990	-16.08	0.0959	-15.64	0.2587	-38.84
0.2125	-34.60	0.24392	-39.22	0.1461	-23.74	0.1386	-22.39	0.2935	-44.68
0.2687	-43.05	0.2659	-42.40	0.1888	-31.41	0.1777	-28.71	0.3260	-49.35
0.3253	-50.76	0.2890	-45.64	0.2290	-38.03	0.2153	-35.03	0.3558	-53.54
0.3509	-54.34	0.3115	-48.62	0.2654	-43.64	0.2506	-40.52	0.3833	-56.72
0.3774	-57.68	0.3330	-51.31	0.3000	-48.49	0.2834	-45.25	0.4087	-58.11
0.4050	-60.63	0.3533	-54.07	0.3318	-52.99	0.3152	-49.62	0.4329	-59.76
0.4307	-62.85	0.3728	-56.22	0.3616	-56.32	0.3445	-53.12	0.4556	-61.59
0.4548*	-64.69*	0.3921	-58.24	0.3892	-59.18	0.3714	-55.89	0.4780	-62.54
0.4769*	-66.70*	0.4106	-59.76	0.4157	-61.54	0.3962	-58.54	0.4987	-63.25
0.4920*	-68.36*	0.4280	-60.96	0.4406*	-63.45*	0.4193	-61.03	0.5190	-63.31
0.5075*	-68.39*	0.4451*	-61.85*	0.4636*	-64.50*	0.4410	-62.38	0.5401	-63.14
0.5232*	-68.96*	0.4619*	-64.19*	0.4848*	-70.75*	0.4628	-63.63		
0.5382*	-63.45*	0.4692*	-65.18*	0.5066*	-71.25*	0.4831	-64.25		
0.5525*	-63.08*	0.4849*	-68.31*	0.5271*	-63.75*	0.5022	-64.72		
0.5664*	-62.40*	0.4999*	-69.41*	0.5460*	-63.66*	0.5204	-64.90		
0.5815*	-61.29*	0.5162*	-69.07*	0.5635*	-63.14*	0.5374	-64.83		
0.5958*	-60.06*	0.5350*	-61.80*			0.5536	-64.61		
0.6092*	-58.82*	0.5526*	-61.92*			0.5694	-63.98		
		0.5695*	-61.39*			0.5856	-63.13		

* The initial mass of gallium placed in the crucible is given under the experimental temperature. Values marked with an asterisk (*) correspond to the formation of a two-phase solid–liquid alloy.

considered to be independent of temperature, and can be given by the following equation:

$$\Delta_{mix}H_m^\circ = x_{Pt}(1 - x_{Pt})\xi(x_{Pt}) \qquad (1)$$

where

$$\xi(x_{Pt}) = (-150.19 - 308.28x + 126.28x^2 + 131.88x^3 - 14.31x^4) \qquad (2)$$

The coefficients have been calculated by the least squares method. The $\xi(x_{Pt})$ function is shown in Fig. 3.
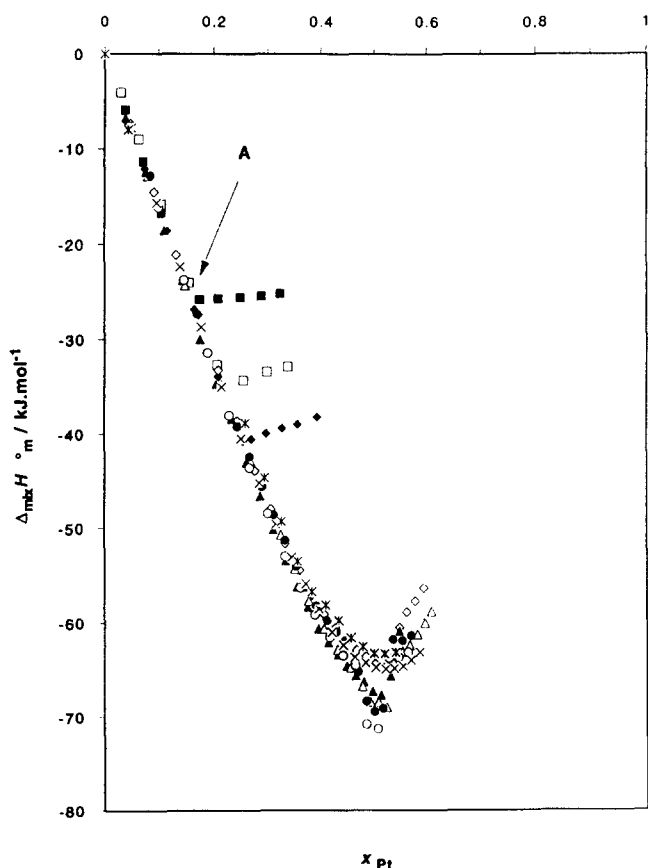
Fig. 2. Experimental values of the enthalpies of formation of liquid and solid + liquid (Pt + Ga) alloys at different temperatures: ■ 1071 K, □ 1125 K, ◆ 1175 K, ◇ 1325 K, ▲ 1350 K, △ 1351 K, ● 1353 K, ○ 1366 K, × 1406 K, × 1465 K.

4.1.2. Molar partial enthalpies

$\Delta_{mix}h^{\circ}_m$(Pt), the partial enthalpy of platinum, can be deduced directly from the experiments. In this case, the experimental partial enthalpies are obtained for the average molar fraction $\bar{x}$, with $\bar{x}(i) = [x_{Pt}(i-1) + x_{Pt(i)}]/2$ (i being number of the addition). In Fig. 3, we have plotted the $\Delta_{mix}h^{\circ}_m$(Pt) $= f(x_{Pt})$ function calculated by

$$\Delta_{mix}h^{\circ}_m(Pt) = \Delta_{mix}H^{\circ}_{m+}(1 - x_{Pt})\delta(\Delta_{mix}H^{\circ}_m)/\delta x_{Pt}$$

$$= (1 - x_{Pt})^2[\xi(x_{Pt}) + x_{Pt}(\delta\xi(x_{Pt})/\delta x_{Pt})] \qquad (3)$$

Moreover, $\Delta_{mix}h^{\circ}_m$(Ga), the partial molar enthalpies of Ga were derived using

$$\Delta_{mix}h^{\circ}_m(Ga) = [\Delta_{mix}H^{\circ}_m - x_{Pt}\Delta_{mix}h^{\circ}_m(Pt)]/(1 - x_{Pt}) \qquad (4)$$

and are also given in Fig. 3.

4.1.3. Limiting molar partial enthalpies

From two series of measurements at 1169 K $(0 < x_{Pt} < 0.010$ and 1180 K $(0 < x_{Pt} < 0.012)$, the partial enthalpies of mixing of Pt supercooled liquid in liquid gallium were determined (Table 2, Fig. 4). The change in the partial enthalpy vs. concentration $\bar{x}$, can also be represented by a linear function:

$$\Delta_{mix}h^{\circ}_m(Pt) = \Delta_{mix}h^{\circ\ \infty}_m(Pt) + \varepsilon_{Pt,Pt}x_{Pt}$$

where $\varepsilon_{Pt,Pt}$ is the factor of interaction between the platinum atoms. In this case, $\Delta_{mix}h^{\circ\ \infty}_m$ (Pt supercooled
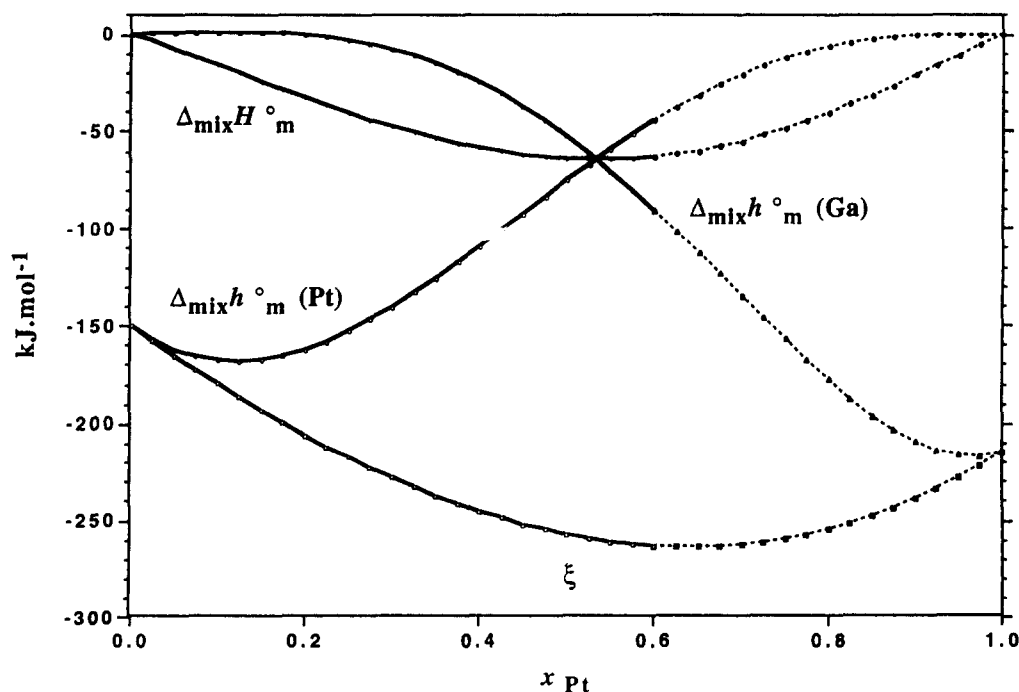

Fig. 3. Variation of the ξ-function and of the integral and partial molar enthalpies of formation vs. x_{Pt}: ——, smoothed curves according to Eqs. (1)–(4); — — —, extrapolated.

Table 2

Experimental partial molar enthalpies (kJ mol^{-1}) of platinum measured at 1169 K and 1180 K, $\bar{x}$ is the average value of the platinum molar fraction.

$T = 1169$ K $m_{Ga} = 4.43340$ g		$T = 1180$ K $m_{Ga} = 4.49013$ g	
$\bar{x}_{Pt}$	$\Delta_{mix}h^{\circ}_{m}(Pt)$	$\bar{x}_{Pt}$	$\Delta_{mix}h^{\circ}_{m}(Pt)$
0.00066	−154.46	0.00075	−150.02
0.00200	−154.22	0.00228	−147.28
0.00342	−155.30	0.00385	−147.94
0.00511	−154.96	0.00542	−146.87
0.00702	−153.84	0.00700	−150.49
0.00900	−154.16	0.00863	−150.38
		0.01035	−153.68
		0.01210	−154.37

The initial mass of gallium placed in the crucible is given under the experimental temperature.

liq. in ∞ liq Ga) is found to be −151 kJ mol^{-1} with a scatter estimated to be less than ±4%. However, by extrapolation of the ξ-function to $x_{Pt} = 1$, the limiting partial molar enthalpy of gallium in supercooled liquid platinum was estimated as $\Delta_{mix}h^{\circ\,\infty}_{m}$ (Ga liq in ∞ supercooled liq Pt) = −215 ± 30 kJ mol^{-1}.

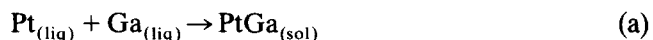### 4.2. Enthalpy of formation and enthalpy of fusion of PtGa

The molar enthalpy of formation and the enthalpy of fusion of the solid PtGa compound were determined by direct reaction calorimetry measurements performed at about 1350 K. Fig. 5 shows the graph of the enthalpy of mixing vs. concentration of the three series. This graph with a negative peak $(L_1 S L_2)$ exhibits four regions.

(i) From $x_{Pt} = 0$ to L_1 $(x_{Pt} = 0.426)$, the same parabolic variation as in the other series is observed, corresponding to the formation of a single liquid alloy.

(ii) In L_1, the precipitation of the PtGa solid phase corresponds to a discontinuity followed by a linear part $L_1 S$.
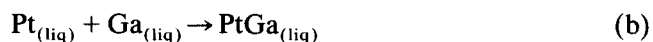
(iii) In S $(x_{Pt} = 0.506)$, the formation of the compound PtGa is achieved and the enthalpy value corresponds to the reaction

$$Pt_{(liq)} + Ga_{(liq)} \rightarrow PtGa_{(sol)} \qquad (a)$$

(iv) From S to L_2, the compound is dissolved by further additions of Pt; at L_2 $(x_{Pt} = 0.442)$ the alloy is liquid again.

(v) Beyond L_2, a parabolic variation of the $\Delta_{mix}H^{\circ}_{m}$ function is observed.

The enthalpy of formation of the solid compound PtGa corresponding to reaction (a) is $\Delta_{for}H^{\circ}_{m}$(PtGa, sol) = −69.5 kJ mol^{-1}. The hypothetical value of the enthalpy of formation of this liquid phase, corresponding to the equation

$$Pt_{(liq)} + Ga_{(liq)} \rightarrow PtGa_{(liq)} \qquad (b)$$

is obtained by interpolation of $\Delta_{mix}H^{\circ}_{m} = f(x_{Pt})$ curve between L_1 and L_2: $\Delta_{mix}H^{\circ}_{m}$ (PtGa,liq) = − 64.4 kJ mol^{-1}, in L^0. Neglecting the change in the heat capacities in the narrow temperature range (1350–
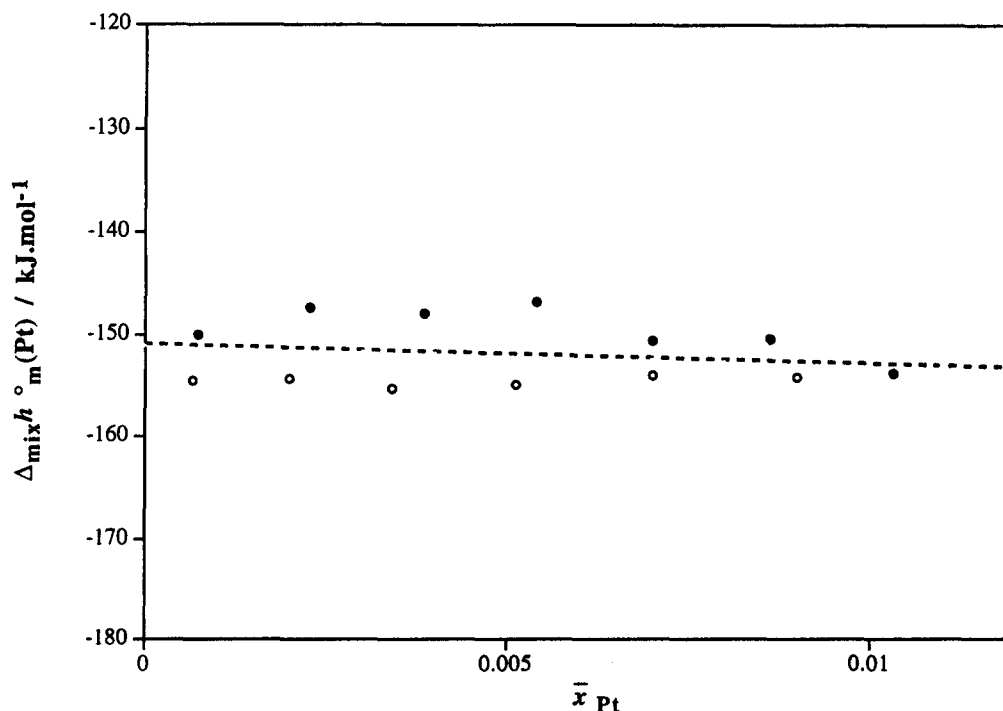

Fig. 4. Partial molar enthalpies of platinum ($\Delta_{mix}h^{\circ}_{m}(Pt) = f(x_{Pt})$) obtained at 1169 K (○) and 1180 K (●) for $0 < x_{Pt} < 0.010$.
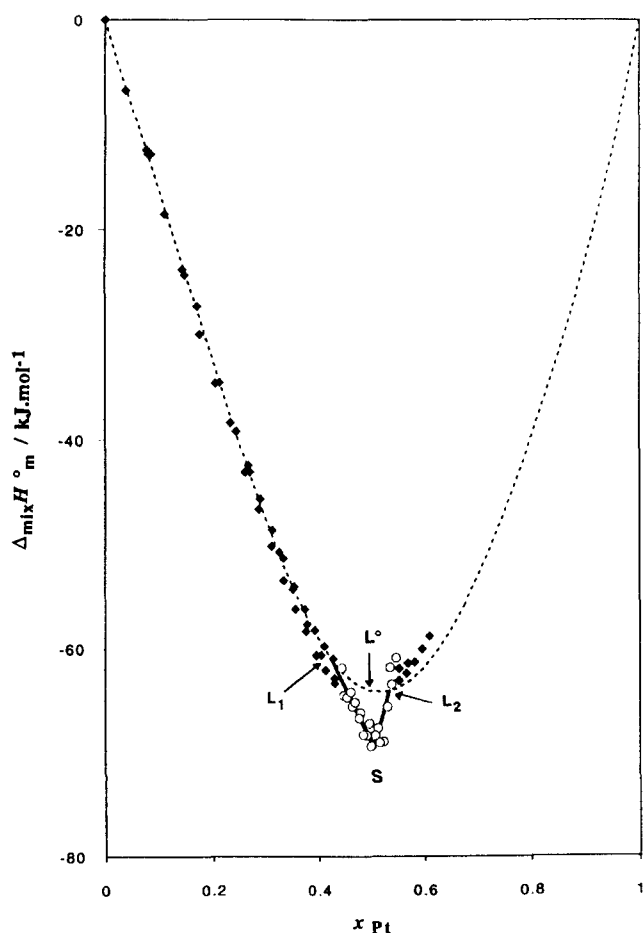
Fig. 5. Integral enthalpies of mixing vs. concentration at 1350 K showing the formation of the solid compound PtGa liquid alloys (◆), two-phase solid–liquid alloys (○), and Eq. (1) (- - -).

Table 3
Coordinates of liquidus points obtained from calorimetric measurements (and bibliographic data [7])

T/K	x_{Pt} (this work)	x_{Pt} [7]
1071	0.15_8	0.18_5
1125	0.21_3	0.23_0
1175	0.25_1	0.28_0
1325	$-^a$	0.42_0
	0.54_4	0.55_0
≈ 1350	0.42_6 (L$_1$)	0.45_5
	0.53_4 (L$_2$)	0.53_0
1366	0.46_9	0.48_0
	0.52_3	0.51_5

^{a} Unknown.

and solid super heated Ga at 1350 K is given as $-56.4 \text{ kJ mol}^{-1}$. The enthalpy of fusion obtained by our experiments was 5.1 kJ mol^{-1}, given an excess enthalpy of fusion for the alloy of about -8 kJ mol^{-1}.

4.3. Liquidus line

In the series of measurements, some breaks occurred in the $\Delta_{mix}H^\circ_m$ curve (for instance point A, Fig. 2) corresponding to the appearance of a two-phase solid–liquid alloy. These points are generally in good agreement with the phase diagram [7] around the PtGa compound, but at lower temperature the uncertainty of our resolution is larger. Our results and the experimental data published by Guex and Feschotte [7] are reported in Table 3.

4.4. Molar heat capacities

The molar heat capacities of two solid compounds (GaPt and Ga$_3$Pt$_5$) were obtained with an accuracy of about 0.5%. The results are gathered in Table 4 with the C_p obtained by Kopp and Neumann law's between 423 K and 763 K. The C_p for pure gallium and platinum were taken from Barin and Knacke [16]: for Ga solid, $C_p = 25.899 \text{ J K}^{-1} \text{ mol}^{-1}$; for Pt solid, $C_p = 24.250 + 5.376 \times 10^{-3}T \text{ J K}^{-1} \text{ mol}^{-1}$. The ΔC_p are slightly negative in the temperature range investigated, corresponding to an arrangement in the solid state.

1337 K), the enthalpy of fusion $\Delta_{fus}H^\circ_m$ (PtGa) can be derived from the previously mentioned measurements by

$$\Delta_{fus}H^\circ_m(\text{PtGa}) = \Delta_{mix}H^\circ_m(\text{PtGa, liq})$$
$$- \Delta_{for}H^\circ_m(\text{PtGa, sol})$$
$$= +5.1 \text{ kJ mol}^{-1}$$

To refer to the solid state, the enthalpies of crystallization of Pt and Ga have to be subtracted in stoichiometric quantities. So

$$\Delta_{for}H^\circ_m(\text{PtGa})_{sol,ref\ to\ sol} = \Delta_{for}H^\circ_M(\text{PtGa})_{sol,ref\ to\ liq}$$
$$- 0.5 . \Delta_{crys}H^\circ_m(\text{Pt})$$
$$- 0.5 . \Delta_{crys}H^\circ_m(\text{Ga})$$

The enthalpy of fusion of Pt is calculated by extrapolating the relative enthalpy of solid at that temperature: $\Delta_{crys}H^\circ_m(\text{Pt}) = -\Delta_{fus}H^\circ_m(\text{Pt}) = -18.72_5$ kJ mol^{-1}. For Ga, the enthalpy of fusion is calculated under the assumption of constant entropy of fusion: $\Delta_{crys}H^\circ_m(\text{Ga}) = -\Delta_{fus}H^\circ_m$ (Ga) = -7.54_0 kJ mol^{-1}. The althalpy of formation referred to solid supercooled Pt

5. Discussion

In Fig. 6 and Table 5 we listed the data of the integral molar enthalpies and free energies of formation of solid and liquid (Pt + Ga) alloys: (i) calculated by Miedema and coworkers [5], (ii) measured by Vogelbein et al. [9], (iii) obtained by direct calorimetry (this work). Observation of the results leads us to make the following remarks.

(a) The enthalpies of formation of solid alloys proposed by Vogelbein et al. are roughly in agreement

Table 4
Experimental molar heat capacities of GaPt and Ga_3Pt_5 compared with the Kopp and Neumann rule

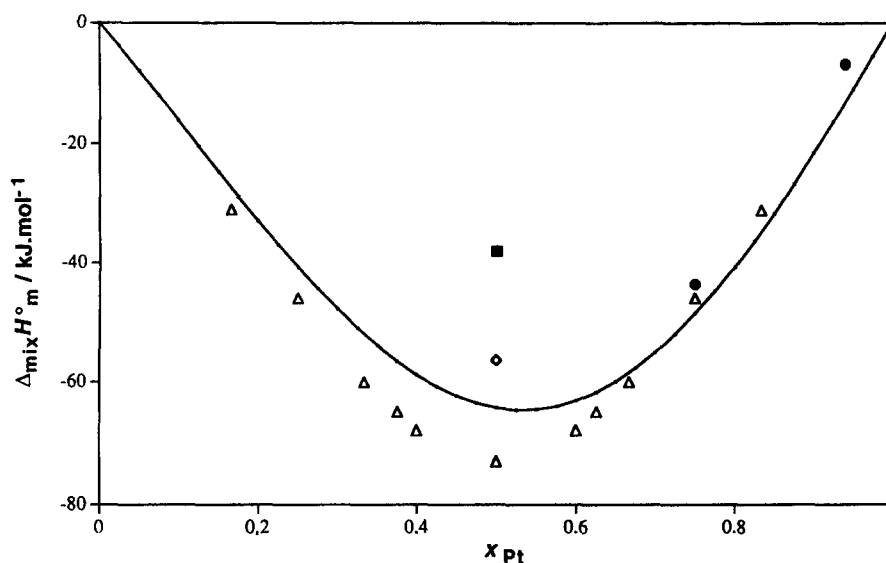| T (K)	$C_p(exp)$ (J K^{-1} (mol^{-1}))	$C_p(add)$ (J K^{-1} (mol^{-1}))	$C_p(exp)$ (J K^{-1} (mol^{-1}))	$C_p(add)$ (J K^{-1} (mol^{-1}))
423	23.51	26.21	25.33	26.29
443	23.93	26.26	26.00	26.36
463	24.21	26.32	25.95	26.42
483	23.85	26.37	25.84	26.49
503	24.13	26.42	26.13	26.56
523	23.74	26.48	26.17	26.63
543	24.54	26.53	25.83	26.69
563	25.55	26.59	25.91	26.76
583	26.04	26.64	26.22	26.83
603	26.08	26.69	25.92	26.89
623	26.50	26.75	24.93	26.96
643	26.00	26.80	24.55	27.03
663	25.99	26.85	25.41	27.10
683	25.67	26.91	25.42	27.16
703	25.41	26.96	25.99	27.23
723	25.16	27.02	25.87	27.30
743	24.89	27.07	25.60	27.37
763	25.22	27.12	25.59	27.43

Fig. 6. Measured and calculated enthalpies of formation of solid and liquid (Pt + Ga) alloys: ——, this work liquid reference; ◇, this work, solid reference; ●, [9] solid reference; △, [5] solid reference; ■, [5] liquid reference.

with our values, but the difference between the values predicted by Miedema is important; the minimum proposed by Miedema is about -73 kJ mol^{-1} for PtGa, when our experimental value is -56.4 kJ mol^{-1}. (b) The discrepancy between experimental and calculated data of the enthalpy of formation in the liquid state is important too (at $x_{Pt} = 0.5$, $\Delta_{mix}H_m^\circ = -38$ kJ mol^{-1} according to Miedema, to be compared with -64.4 kJ mol^{-1}). Moreover, the value of the limiting partial molar enthalpy of platinum in gallium proposed by Miedema is -148 kJ mol^{-1}, whereas this work shows -151 kJ mol^{-1} referred to liquid Pt. However, there is a fair agreement between our

experimental liquid values and the enthalpies of formation of solid alloys calculated by Miedema. Similar behavior has been detected for the (Pd + In), (Pt + In) and (Pd + Ga) systems too. For alloys composed of a transition metal and a non-transition metal, Miedema has introduced the R-factor, taking into account the interaction of d-type electrons with s- and p-type electrons. To calculate the enthalpies of mixing Miedema proposed the relation $R_{liquid\ phase} = 0.73R_{solid\ phase}$. However, our experimental results for (TM + In) and (TM + Ga) alloys show excellent agreement with the calculations, if the prefactor $R_{solid\ phase}$ is taken as very close to unity.

Table 5
Measured and calculated values of the enthalpies of formation (kJ mol^{-1}) of solid and liquid (Pt + Ga) alloys

x_{Pt}	Calculated $\Delta_{mix}H^{\circ}_m$ solid reference [5]	Calculated $\Delta_{mix}H^{\circ}_m$ liquid reference [5]	Experimental $\Delta_{mix}H^{\circ}_m$ solid reference [9]	Experimental $\Delta_{mix}G^{\circ}_m$ (1100 K) solid reference [10]
0.167	−31			
0.250	−46			
0.300				−45.4
0.333	−60			−47.4
0.375	−65			
0.400	−68			−51.1
0.500	−73	−38		−56.3
0.600	−68			
0.625	−65			−50.4
0.667	−60			−46.5
0.750	−46		−43.7	−37.5
0.833	−31			
0.940	−11		−6.7	

Comparing the enthalpies of mixing of the (Pd + Ga) and (Pt + Ga) systems, a pronounced asymmetry is observed in the enthalpy of mixing vs. concentration curve for (Pd + Ga), (minimum at $x_{Pd} = 0.6$ and -70.4 kJ mol^{-1}) whereas (Pt + Ga) is characterized by a nearly symmetrical curve ($x_{Pt} = 0.52$ and -64.5 kJ mol^{-1}). However, the values of the limiting partial enthalpies of Pd and Pt (-144 and -151 kJ mol^{-1}) are quite similar but, surprisingly, the limiting partial enthalpy of Pt is more exothermic than that of palladium, even when inverted for the enthalpy of mixing.

The same behavior is observed for the Pd + In (asymmetric curve) and Pt + In (symmetric curve) systems too. Thus the (TM + Ga) alloys are more exothermic than the (TM + In) alloys (Fig. 7).

Hayer and Bros [17] have proposed a new function, the Fermi-enthalpy defined as $H_F = [\Delta h^{\circ}_m(a) - \Delta h^{\circ}_m (b) - \Delta h^{\circ\,\infty}_m (a)]$ where Δh°_m (a) and Δh°_m (b) are the partial molar enthalpies of a (a ≡ sp elements: In, Ga) and b(b ≡ transition metals: Pt, Pd) respectively and $\Delta h^{\circ\,\infty}_m$ (a) is the limiting partial enthalpy of a. In some ways, the Fermi enthalpy represents the change in the Fermi energy on alloying, indicating by the slope the density of states (DOS) of the alloy. A steep slope corresponds to a low DOS, whereas a flat slope indicates a high DOS at the Fermi energy.

For (Pd + In) as for (Pd + Ga) alloys with $x_{Pd} < 0.33$, a nearly horizontal part was detected. From stoichiometric reasons, this phenomenon was interpreted as a limit for the transfer of electrons from In or Ga to Pd to 2 electrons at most. The Fermi energy for (Pt + In) reveals a maximum at about $x_{Pt} = 0.17$ corresponding to the transfer of about 2.5 electrons. For (Pt + Ga), we can observe a maximum for $x_{Pt} = 0.125$ or 2.6 electrons. One can assume that 2.5 electrons at most are transferred in the direction from In or Ga to Pt (Fig. 8).
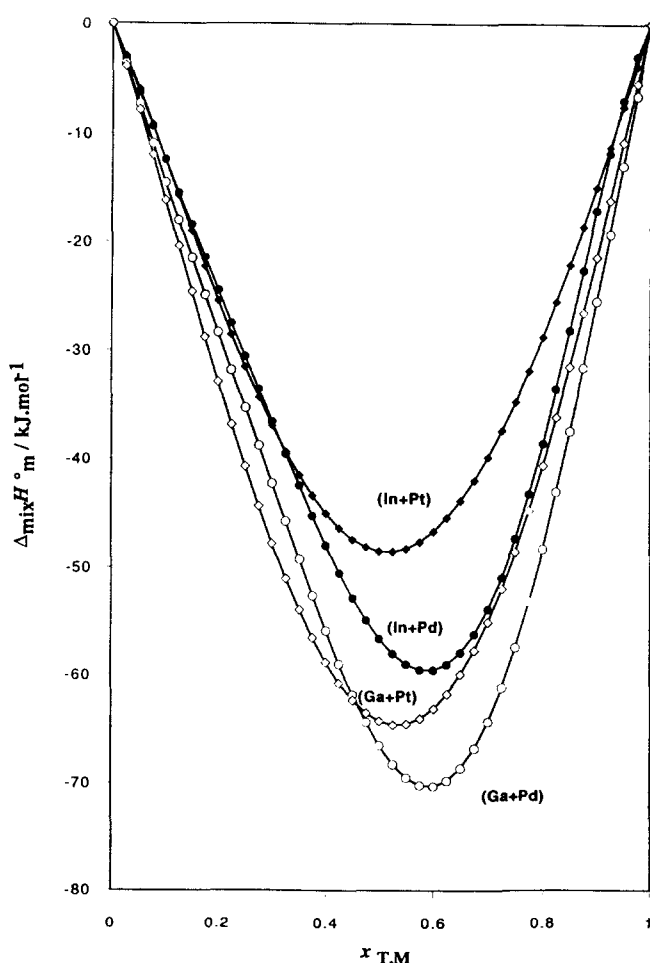

Fig. 7. Enthalpy of formation of the (Pd + Ga)(○), (Pt + Ga)(◇), (Pd + In)(●) and (Pt + In)(◆) liquid alloys (TM is Pd or Pt).

The hypothesis of an electronic transfer from sp metals to transition metals can be connected with the Al contribution of between 2.6 and 3 electrons per Al atom to the Pd conduction band, proposed by Gugla
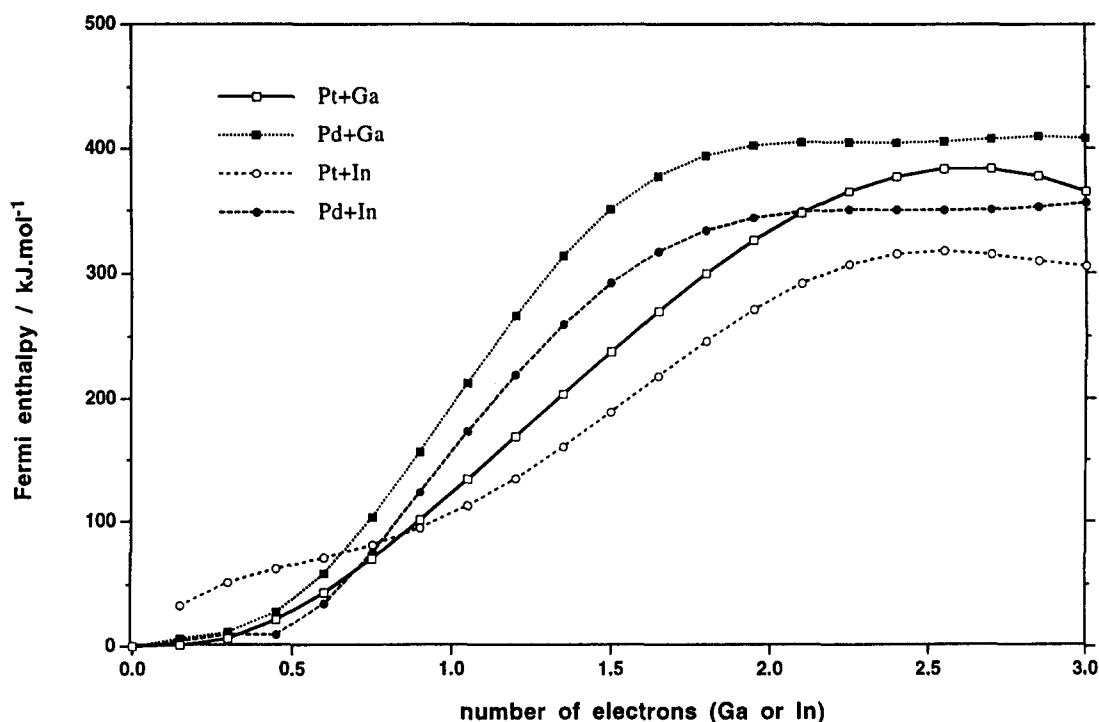
Fig. 8. Change in the Fermi energy for the systems (Pd + Ga), (Pt + Ga), (Pd + In) and (Pt + In).

et al. [18] and confirmed by XPS measurements realized on (Pd + Al) alloys by Fuggle et al. [19].

(Pd + Ga), (Pd + In), (Pt + Ga) and (Pt + In) are interpreted in terms of an electron transfer from gallium or indium to the d-orbital of the transition metal.

6. Conclusion

In summary, the calorimeter measurements performed between $1071 < T/K < 1465$ provided the following information. The molar enthalpy of formation of the liquid (Pt + Ga) system, independent of temperature, can be described by the equation $\Delta_{mix}H^\circ_m = x_{Pt} (1 - x_{Pt})\xi(x_{Pt})$ kJ mol^{-1} with $\xi(x_{Pt}) = -150.19 - 308.28x_{Pt} + 126.28x_{Pt^2} + 131.88x_{Pt^3} - 14.31x_{Pt^4}$ with a minimum $\Delta_{mix}H^\circ_m = -64.5$ kJ mol^{-1} at $x_{Pt} = 0.52$. The partial molar enthalpies of platinum have been measured in the gallium-rich region and the limiting value has been extrapolated: $\Delta_{mix}h^{\circ\,\infty}_m$ (Pt supercooled liq. in ∞ liq Ga) = -151 ± 5 kJ mol^{-1}. Using the integral and partial enthalpies, the molar partial enthalpies of gallium have been calculated leading to the following value: $\Delta_{mix}h^{\circ\,\infty}_m$ (Ga liq in ∞ Pt supercooled liq) = -215 ± 30 kJ mol^{-1}. The enthalpies of formation of the (TM + Ga) liquid systems are more exothermic than those of the (TM + In) systems. Moreover, the $\Delta_{mix}H^\circ_m = f(x)$ curves are strongly asymmetrical for the (Pd + Ga) and (Pd + In) systems and nearly symmetrical for the (Pt + Ga) and (Pt + In) systems. In the solid state, experimental and predicted data (using Miedema's model) show a slight discrepancy.

The highly negative enthalpies of formation of the

Acknowledgments

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