

Thermodynamic properties of Pt₅La, Pt₅Ce, Pt₅Pr, Pt₅Tb and Pt₅Tm intermetallics

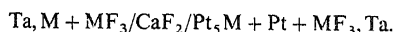
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Abstract. The Gibbs' energies of formation of Pt₅La, Pt₅Ce, Pt₅Pr, Pt₅Tb and Pt₅Tm intermetallic compounds have been determined in the temperature range 870–1100 K using the solid state cell:



The reversible emf of the cell is directly related to the Gibbs' energy of formation of the Pt₅M compound. The results can be summarized by the equations:

$$\Delta G_f^\circ \langle \text{Pt}_5\text{La} \rangle = -373,150 + 6.60 T (\pm 300) \text{ J mol}^{-1}$$

$$\Delta G_f^\circ \langle \text{Pt}_5\text{Ce} \rangle = -367,070 + 5.79 T (\pm 300) \text{ J mol}^{-1}$$

$$\Delta G_f^\circ \langle \text{Pt}_5\text{Pr} \rangle = -370,540 + 4.69 T (\pm 300) \text{ J mol}^{-1}$$

$$\Delta G_f^\circ \langle \text{Pt}_5\text{Tb} \rangle = -372,280 + 4.11 T (\pm 300) \text{ J mol}^{-1}$$

$$\Delta G_f^\circ \langle \text{Pt}_5\text{Tm} \rangle = -368,230 + 4.89 T (\pm 300) \text{ J mol}^{-1}$$

relative to the low temperature allotropic form of the lanthanide element and solid platinum as standard states. The enthalpies of formation of all the Pt₅M intermetallic compounds obtained in this study are in good agreement with Miedema's model. The experimental values are more negative than those calculated using the model. The variation of the thermodynamic properties of Pt₅M compounds with atomic number of the lanthanide element is discussed in relation to valence state and molar volume.

Keywords. Platinum–lanthanide intermetallic compounds; Gibbs' energy of formation; enthalpy of formation; entropy of formation; systematics.

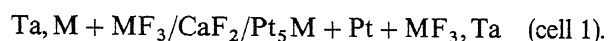
1. Introduction

The platinum-rich intermetallic compounds of lanthanide elements are of interest from the practical as well as the theoretical point of view. It is known (Bronger 1967) that the oxides of most lanthanide elements can be reduced in the presence of platinum by dry hydrogen or ammonia at temperatures above 1473 K resulting in the formation of Pt₅M compounds, where M represents a lanthanide element. This points to the very high stability of the intermetallic phases. Based on the experimental observation of Bronger (1967), Wengert and Spanoudis (1974) have estimated the upper limit on the Gibbs' energy of formation of some Pt₅M compounds. It is possible to recover some lanthanide metals from the Pt₅M intermetallics by sublimation at higher temperatures. In order to compute the optimum temperatures for the recovery of the lanthanides more accurate thermodynamic data are required.

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All the rare earth elements except perhaps Ce can be described by a localized 4*f* (core) electron model. Except for the elements Eu and Yb which are divalent in their elementary metallic state, other rare earth metals are trivalent. They can be treated as having three conduction electrons per atom and M^{3+} ionic cores. Platinum forms a series of intermetallic compounds with each lanthanide metal (Iandelli and Palenzona 1981; Moffatt 1985; Massalski 1986). The compound with the highest concentration of Pt has the formula Pt_5M for *M* ranging from La to Tm. For Yb and Lu the compound having the highest concentration of Pt is Pt_3M , which has the Cu_3Au structure (Bronger 1967; Moffatt 1985; Massalski 1986). Pt_5M compounds containing the lighter lanthanides crystallize in the hexagonal $CaCu_5$ structure (Bronger 1967). For $M=Sm, Eu$ and Gd the structure is similar, but the powder pattern contains more reflections. The structure has rhombic symmetry (Bronger 1967). A further small change in structure occurs at Tb. The lanthanide contraction is manifested by the shrinkage in the *a*- or the *a*- and *b*-axes, whereas the *c*-axis becomes larger. The crystal structures of Pt_5M compounds containing the heavier rare earth metals have not been fully elucidated.

Since the literature does not contain any report about thermodynamic measurements on Pt_5M compounds containing lanthanides, solid state galvanic cell measurements were undertaken on systems containing La, Ce, Pr, Tb and Tm in the temperature range 870–1100 K. The galvanic cell had the configuration represented by



Single crystal CaF_2 was used as the solid electrolyte and Ta wire as the electrical lead to the electrodes. The emf of cell I directly gives the Gibbs' energy of formation of Pt_5M without the use of any auxiliary data. The Gibbs' energies of formation of Pt_5M compounds ($M=Nd, Sm, Eu, Gd, Dy, Ho, Er$) have been measured recently (Jacob and Waseda 1990).

2. Experimental

2.1 Materials

The purity of the starting materials was 99.9% for the lanthanide metals and 99.99% for Pt. The Pt_5M intermetallic compounds were prepared both by arc melting on a water-cooled copper hearth ($M=Tb, Tm$) and by solid state reaction of powders under prepurified argon ($M=La, Ce, Pr$). High purity argon was further dried over P_2O_5 and deoxidized by passage through granules of Ti at 1173 K. The alloy buttons were remelted two or three times to ensure homogeneity. Weight losses were found to be negligible. The final composition of the compounds were confirmed by chemical analysis. In the powder technique synthesis, an intimate mixture of metal powders in the required ratio was pressed into pellets and sealed under high purity argon in a molybdenum crucible. The crucible was heated under argon to a temperature of 1000 K. The reactions were exothermic. The intermetallic compounds were annealed under high vacuum at 1100 K for 300 ks. Formation of the Pt_5M compounds was confirmed by X-ray diffraction. Single crystals of CaF_2 of 99.999% purity were obtained from the Harshaw Chemical Company. The lanthanide fluorides used in the electrodes were of 99.9% purity.

2.2 Apparatus and procedure

The emf of cell 1 was measured as a function of temperature from 870 to 1100 K for $M = \text{La, Pr, Tb}$ and Tm . Because of the low melting point of Ce, the measurements were restricted to 1070 K for this system. The emf response was very sluggish at temperatures below 870 K. At temperatures above 1120 K there was evidence of reaction between CaF_2 and rare earth fluorides. The intermetallics were pulverized to -300 mesh and mixed with powders of Pt and rare earth fluorides in the molar ratio 2:1:1. The mixture was compacted into pellets and sintered under prepurified argon at 1200 K. The reference electrode was prepared by compacting an intimate mixture of the lanthanide metal and its coexisting fluoride in the molar ratio 2:1 and sintering under prepurified flowing argon gas at 1100 K for La and Pr, 1050 K for Ce and 1300 K for Tb and Tm.

A schematic diagram of the apparatus is shown in figure 1. The electrode pellets were spring-loaded on either side of a transparent single crystal of CaF_2 . Small Ta foils, spot-welded to Ta wire, were pressed against the electrodes. The pellets and Ta foils were held together under pressure through a system consisting of springs, an alumina rod and a flat-bottomed alumina tube with a section cut away parallel to its axis, as shown in the figure. The cell was enclosed in an outer alumina tube and suspended inside a vertical resistance heated furnace. The top and bottom ends of the outer alumina tube were closed with gas-tight brass heads with provision for gas inlet and outlet and insulated electrode and thermocouple connections. The cell was maintained under flowing, pre-purified argon gas at a pressure of 1.02×10^5 Pa. The apparatus was evacuated and refilled with argon twice at room temperature and at 600 K. Internal getters of zirconium were placed adjacent to the electrodes to scavenge residual oxygen from the argon gas. Mixed potentials arising from the oxidation of

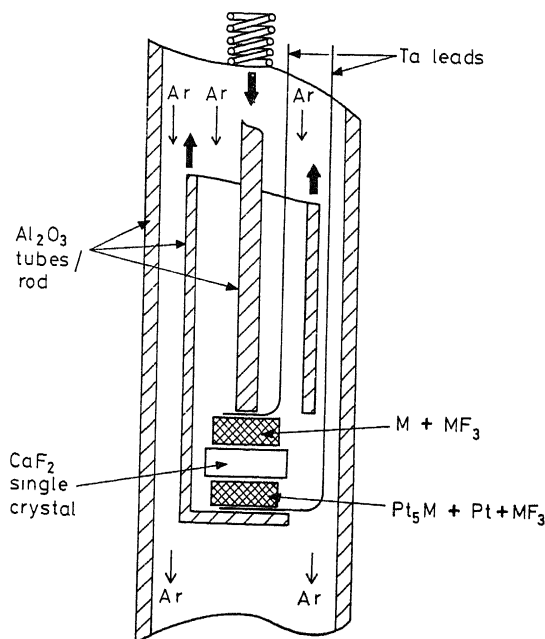


Figure 1. A schematic diagram of the emf apparatus.

the rare earth metal at the electrodes by residual oxygen in the inert gas was encountered in preliminary studies without the use of internal getters. Even though the inert gas was deoxidized prior to its admission into the emf apparatus, oxygen-containing species were apparently picked up by the gas stream before it passed over the electrodes. Desorption of O_2 , CO , CO_2 and H_2O species from the ceramic tubes was one probable cause of the contamination. Flux of oxygen through the outer alumina tube because of the electrochemical permeability of the ceramic was perhaps another cause of contamination. Internal getters were effective in deoxidation of the inert gas *in situ*. A Kanthal tape, wrapped around the outer alumina tube housing the cell, was earthed to minimize induced emf on cell leads from the furnace winding. The emf across the Ta leads was measured with a high impedance (10^{12}) digital voltmeter. The cell registered steady emfs in 7 to 30 ks after the attainment of thermal equilibrium depending on the temperature of measurement.

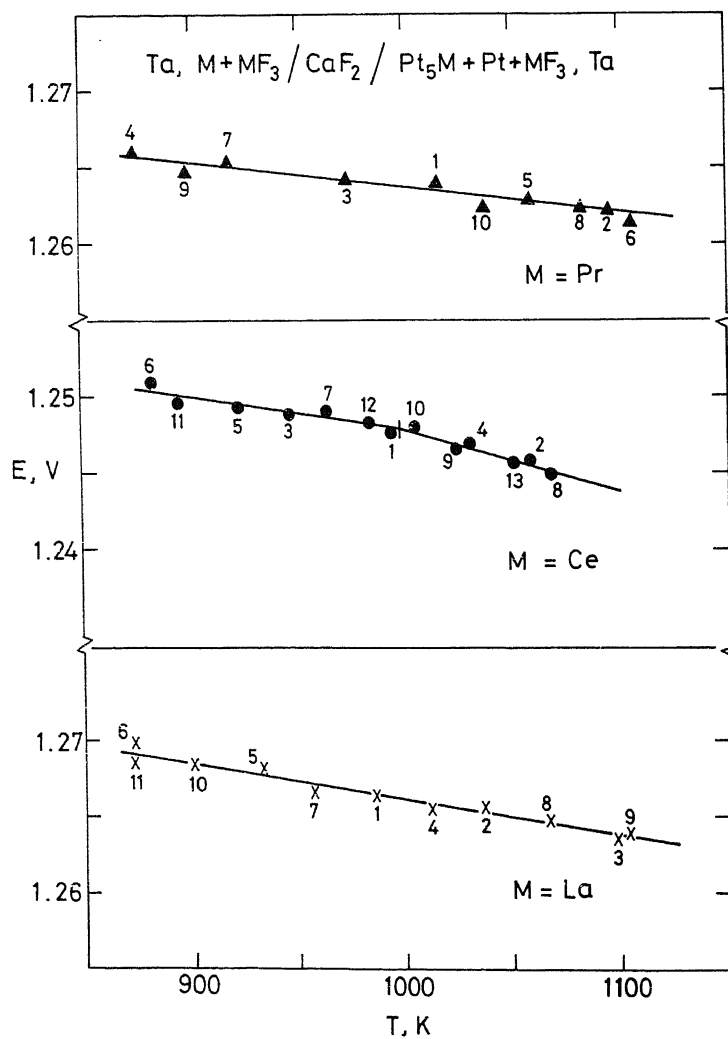


Figure 2. The temperature dependence of the emf of cell 1 for M=La, Ce and Pr.

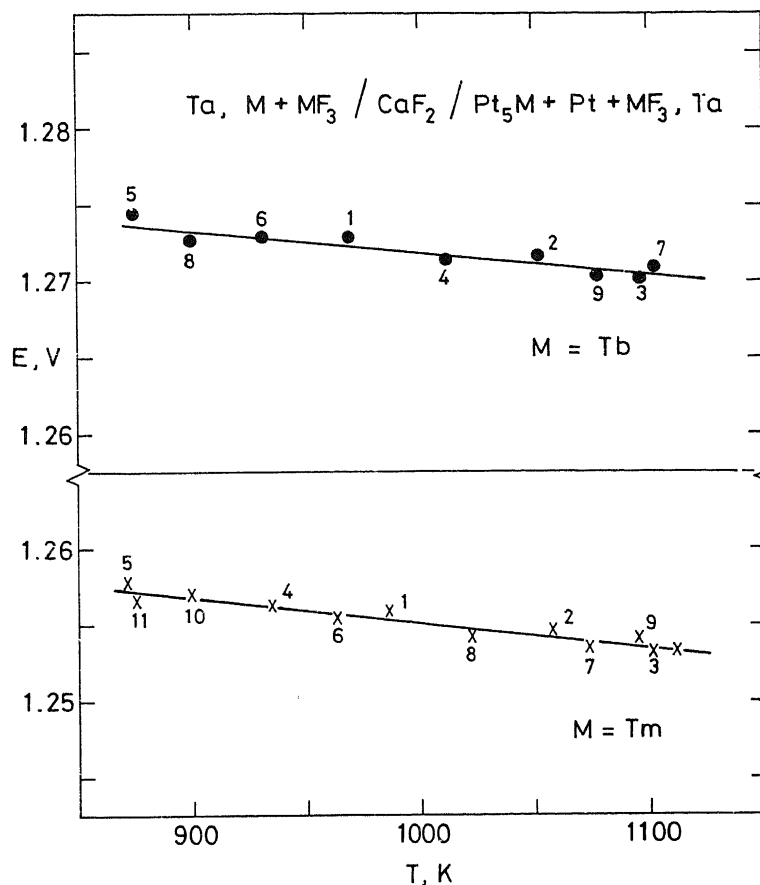


Figure 3. The variation of the emf of cell 1 for $M = Tb$ and Tm with temperature.

The reversibility of the emf was checked by passing small currents ($\sim 40 \mu A$) in either direction through the cell for 0.3 ks and verifying that the emf returned to the steady value before each microcoulometric titration. The emf was independent of the flow rate of the inert gas through the apparatus in the range 2.5 to 6 ml s^{-1} . The emf of cell 1 was reproducible on temperature cycling to $\pm 1 \text{ mV}$. The temperature of the cell was measured by a Pt/Pt-13% Rh thermocouple and controlled to $\pm 1 \text{ K}$. At the end of each experiment the electrodes were examined by X-ray diffraction. There was no apparent change in the phase composition of the electrodes during emf measurement.

3. Results

The variation of the emf of cell 1 with temperature is shown in figures 2 and 3 for $M = La, Ce, Pr, Tb, Tm$. The magnitude of the emf for the five systems is similar. The emf decreases slightly with increasing temperature for all systems investigated. Within experimental error the emf is a linear function of temperature for systems containing La, Pr, Tb and Tm. For the Ce system there is a break in the curve at 999 K, corresponding to phase transition in metallic Ce. Phase transition for Pr occurs at 1068 K.

Table 1. Expressions for the EMF and Gibbs' energy of formation of Pt₅M phases.

Lanthanide element (M)	Temperature range (K)	emf of cell 1 (± 1)(mV)	$\Delta G_f^\circ \langle \text{Pt}_5\text{M} \rangle$ (± 300)(J mol ⁻¹)
La	870–1100	1,289–0.0228 T	– 373,150 + 6.60 T
Ce	870–999	1,268–0.0200 T	– 367,070 + 5.79 T
Ce	999–1070	1,278–0.0304 T	– 370,060 + 8.79 T
Pr	870–1100	1,280–0.0162 T	– 370,540 + 4.69 T
Tb	870–1100	1,286–0.0142 T	– 372,280 + 4.11 T
Tm	870–1100	1,272–0.0169 T	– 368,230 + 4.89 T

However, since this is close to the upper temperature limit of measurement a change in slope is not apparent. Equations for the emf, obtained by the least-mean squares regression analysis of experimental data, are given in table 1. The error limits correspond to twice the standard deviation.

Pure CaF₂ is a predominantly fluorine ion conductor over a wide range of fluorine partial pressures and temperatures. At high temperature it begins to exhibit electronic conduction at fluorine potentials close to that corresponding to the decomposition of CaF₂ (Delcet *et al* 1978). At the fluorine potentials established by the electrodes during this investigation, the average ionic transport number in CaF₂ is greater than 0.99. The emf of the galvanic cell can therefore be related to the Gibbs' energy change for the virtual cell reaction. The emf directly gives the chemical potential of the lanthanide element (M) in the phase mixture Pt₅M + Pt,

$$\Delta\mu_M = RT \ln a_M = -\eta FE \quad (1)$$

where η is the number of electrons associated with the electrochemical reaction and F is the Faraday constant. The value of η is 3 for cell 1. The standard Gibbs' energy of formation of MPt₅ intermetallics is equal to the chemical potential of M in the two-phase mixture Pt₅M + Pt.



$$\Delta G_f^\circ = \Delta\mu_M(\text{Pt}_5\text{M} + \text{Pt}). \quad (3)$$

The Gibbs' energies of formation of all Pt₅M compounds obtained in this study are summarized in table 1. All the compounds exhibit comparable stabilities.

The values of the entropy of formation of Pt₅M compounds are all negative, except for Eu, varying from –4.1 to –8.8 J mol⁻¹ K⁻¹. These small negative values are consistent with the large negative enthalpies of formation of Pt₅M compounds. The vibrational frequencies of atoms in the intermetallic compounds are probably higher than in the component solid metals. In the case of Pt₅Eu the entropy of formation is 5 J mol⁻¹ K⁻¹ (Jacob and Waseda 1990b). A small positive contribution may arise from the transformation of divalent Eu in pure metal to the trivalent state in Pt₅Eu. Because of the small values for the entropy of formation, the Gibbs' energy of formation is only a weak function of temperature.

4. Discussion

The Gibbs' energy of formation of lanthanide Pt₅M compounds at 1000 K is plotted in figure 4 as a function of atomic number. The data for M=Nd, Sm, Eu, Gd, Dy, Ho

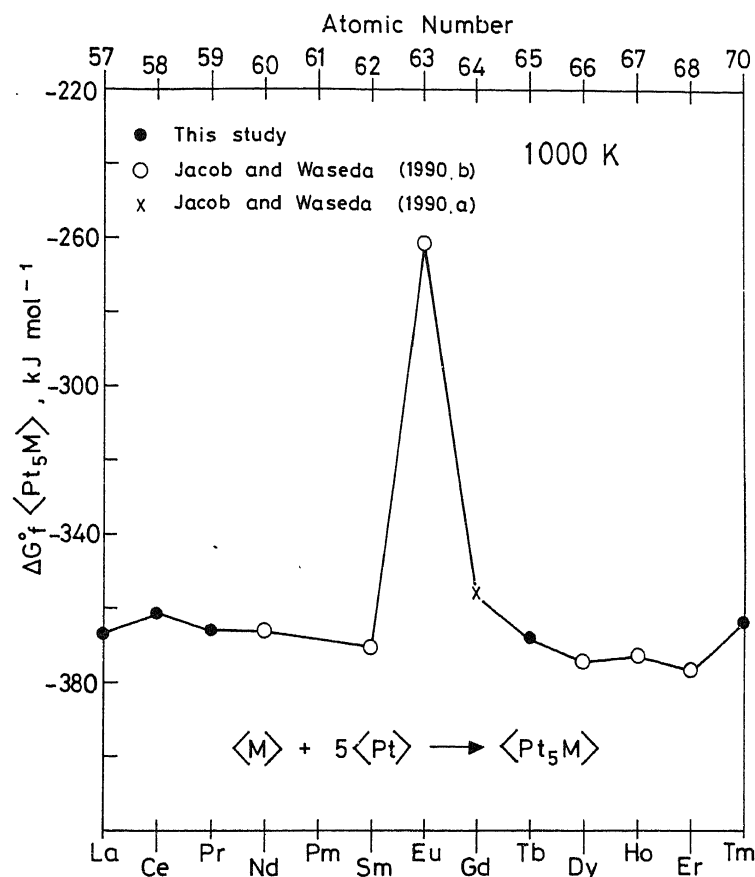


Figure 4. The Gibbs' energy of formation of lanthanide Pt_5M compounds as a function of atomic number.

and Er are from recent emf measurements (Jacob and Waseda 1990). It is seen that the Gibbs' energy of formation of Pt_5Eu is significantly more positive than those for the other lanthanide Pt_5M compounds. Magnetic susceptibility and Mössbauer spectroscopic studies of de Graaf *et al* (1980) show that Eu is trivalent in Pt_5Eu and becomes a mixed valence compound in the solid solution based on Pt_2Eu . The lattice dimensions and close similarity of the compounds Pt_2Eu_5 , Pt_2Eu_3 and Pt_4Eu_5 to those of divalent calcium and strontium suggest that the valency of Eu is two for Eu-rich compositions. In the pure metal Eu is divalent and as a consequence it may be considered as a member of the alkaline-earth group rather than of the trivalent lanthanide group. The molar volume and magnetic behaviour of Eu is different from that expected for a trivalent lanthanide metal. The energy difference between trivalent and divalent modification of Eu has been discussed from an experimental point of view by Gschneidner (1969) and Bayanov and Afanas'ev (1973). The energy difference is found, for instance, by comparing the enthalpy of formation of EuCl_2 with the estimated value for EuCl_3 . The heat of formation of EuCl_3 will be similar to that of the neighbouring element Gd. The transformation energy can also be obtained from the difference in the enthalpy of sublimation of lanthanide metals together with spectroscopic data. As a result Gschneidner (1969) obtains a value of

Table 2. Values of electronegativity (ϕ'), atomic volume (V), and electron density at the Wigner-Seitz atomic cell boundary (η_{ws}) for different elements.

Element	ϕ' (volts)	$\eta_{ws}^{1/3}$ (d.u.) ^{1/3}	$V^{2/3}$ (cm ²)	α
Pt	5.65	1.78	4.36	0.04
La	3.17	1.18	7.98	0.07
Ce	3.18	1.19	7.76	0.07
Pr	3.19	1.20	7.56	0.07
Tb	3.21	1.22	7.20	0.07
Tm	3.22	1.23	6.90	0.07

Reference: Niessen *et al* (1983).

96.2 kJ g-at⁻¹ as the average value of the energy difference between divalent and trivalent modifications of Eu. Bayanov and Afanas'ev (1973) suggest a value of 92 kJ g-at⁻¹. This energy required for the promotion of divalent Eu to the trivalent state accounts for the less negative Gibbs' energy of formation of Pt₅Eu as compared to other Pt₅M lanthanide intermetallics.

The experimental data on the enthalpy of mixing obtained in this study can be compared with the charge transfer model of Miedema *et al* (1975). According to the model the enthalpy of formation of a phase A_{1-x}B_x from metals A and B can be calculated from listed values of electronegativities (ϕ'), atomic volumes (V) and electron densities at the Wigner-Seitz atomic cell boundaries (η_{ws}).

$$\Delta H_f = 2f(x)[(1-x)V_A^{2/3} + xV_B^{2/3}] \frac{-P(\Delta\phi')^2 + Q(\Delta\eta_{ws}^{1/3})^2}{(\eta_{ws}^A)^{-1/3} + (\eta_{ws}^B)^{-1/3}}, \quad (4)$$

where $P = 14.1$ and $Q = 132.54 V^2/(\text{d.u.})^{2/3}$ are constants of the model (Bouten and Miedema 1980; Niessen *et al* 1983) and,

$$f(x) = C_A^S C_B^S [1 + 8(C_A^S C_B^S)^2], \quad (5)$$

$$C_A^S = (1-x)V_A^{2/3}(\text{alloy})[(1-x)V_A^{2/3}(\text{alloy}) + xV_B^{2/3}(\text{alloy})]^{-1}, \quad (6)$$

$$V_A^{2/3}(\text{alloy}) = V_A^{2/3}(\text{pure})\{1 + (\phi'_A - \phi'_B)\alpha f(x)/C_A^S\}. \quad (7)$$

The volume of a component in the alloy is different from its volume in the pure state because of charge transfer effects. The constant α is derived from experimental volume contraction in compounds. The values for ϕ' , V , η_{ws} and α for the different elements used in the calculation are listed in table 2.

The comparison of the enthalpies of formation of Pt₅M compounds obtained from Miedema's model and this study is provided in table 3. It is seen that Miedema's model predicts the enthalpy of formation of Pt₅M compounds involving lanthanide elements with useful accuracy. Small changes in the values for the model parameters ϕ' and η_{ws} can alter the predicted values significantly. The model parameters have been refined during the course of time (Miedema *et al* 1975; Bouten and Miedema 1980; Niessen *et al* 1983). The uncertainty in the model prediction is at least ± 20 kJ mol⁻¹. The good agreement between Miedema's model and experimental data suggests the absence of significant 4f involvement in bonding. Contributions

Table 3. Comparison between the second-law enthalpy of formation of lanthanide Pt₅M compounds and Miedema's model.

Compound	Second law $\Delta H_f^\circ\langle\text{Pt}_5\text{M}\rangle$ (kJ mol ⁻¹)	Miedema's model $\Delta H_f^\circ\langle\text{Pt}_5\text{M}\rangle$ (kJ mol ⁻¹)
Pt ₅ La	-373.2 (± 4)	-355 (± 20)
Pt ₅ Ce	-367.1 (± 4)*	-355 (± 20)
Pt ₅ Pr	-370.5 (± 4)	-356 (± 20)
Pt ₅ Tb	-372.3 (± 4)	-356 (± 20)
Pt ₅ Tm	-368.2 (± 4)	-350 (± 20)

*With respect to solid Pt and γ -Ce as standard states.

Table 4. Comparison between the Gibbs' energies of formation of Pt₅M compounds obtained in this study and the limits suggested by Wengert and Spanoudis.

Compound	Temperature (K)	$\Delta G_f^\circ\langle\text{Pt}_5\text{M}\rangle$ (kJ mol ⁻¹) ^a	$\Delta G_f^\circ\langle\text{Pt}_5\text{M}\rangle$ (kJ mol ⁻¹) ^b
Pt ₅ La ⁺	1473	-361.1 (± 0.5)	< -160.7
Pt ₅ Ce ⁺	1473	-355.1 (± 0.5)	—
Pt ₅ Pr ⁺	1473	-360.9 (± 0.5)	—
Pt ₅ Tb*	1473	-366.2 (± 0.5)	< -298.7
Pt ₅ Tm*	1473	-361.0 (± 0.5)	< -313.8

^aThis study; ^bWengert and Spanoudis (1974)

⁺ with respect to liquid lanthanide metal and solid platinum as standard states,

* with respect to solid lanthanide metal and solid platinum as standard states.

arising from the hybridization of 4*f* wave functions with the bonding 5*d* and 6*s* electrons are not included in Miedema's model.

In the localized 4*f* (core) electron model for Ce there is a choice between trivalent modification (4*f*¹5*d*¹6*s*²) and tetravalent one (4*f*⁰5*d*²6*s*²). The difference in the enthalpy of formation of Pt₅Ce from trivalent and tetravalent Ce ($\Delta H_f^\circ\langle\text{Pt}_5\text{Ce}^{3+}\rangle - \Delta H_f^\circ\langle\text{Pt}_5\text{Ce}^{4+}\rangle$) is 149 kJ mol⁻¹ according to Miedema's model. However, the enthalpy associated with the promotion of Ce metal from the trivalent to tetravalent state has been estimated at 209 kJ mol⁻¹ by Bayanov and Afanas'ev (1973). Based on more recent thermochemical data, de Boer *et al* (1979) have revised the value to 240 kJ mol⁻¹. It would thus appear that Ce is trivalent in Pt₅Ce. The strong magnetic character (Lucken and Bronger 1973) and atomic size (Bronger 1967) of Ce in Pt₅Ce also suggest the trivalent state. However, de Boer *et al* (1979) caution against the general acceptance of a model in which the 4*f* electron in Ce is treated as a core electron. According to them the information on different magnetic behaviour and molar volume of Ce in its intermetallic compounds suggest that the 4*f* electrons can be considered as belonging to the conduction band and contributing to cohesive energy.

The upper limits for the Gibbs' energy of formation of Pt₅M compounds suggested by Wengert and Spanoudis (1974) based on the experiments of Bronger (1967) are

listed in table 4 in comparison with the data obtained in this study. The estimated upper bounds are compatible with the direct experimental information. The present results are extrapolated to 1473 K using thermodynamic data for phase change for La, Ce and Pr from Pankratz (1982).

5. Conclusion

Direct experimental data on Gibbs' energy of formation of five lanthanide Pt_5M compounds have been generated using galvanic cells incorporating single crystal CaF_2 as the solid electrolyte. The enthalpy and entropy of formation of Pt_5M intermetallics are derived from the emf data. The enthalpy of formation obtained from experiment compares well with the predictions of Miedema's model (Miedema *et al* 1975; Bouten and Miedema 1980; Niessen *et al* 1983). The Gibbs' energy and enthalpy of formation of Pt_5Eu compound is substantially less negative than values obtained for other lanthanide Pt_5M compounds. The energy required to promote divalent Eu to the trivalent state accounts for the lower stability of Pt_5Eu .

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