GIBBS ENERGIES OF FORMATION OF RARE EARTH MPt$_5$ COMPOUNDS

K.T. JACOB

Department of Metallurgy, Indian Institute of Science, C.V. Raman Avenue, Bangalore 560 012 (India)

Y. WASEDA

Institute of Mineral Dressing and Metallurgy (SENKEN), Tohoku University, Sendai 980 (Japan)

(Received 2 January 1990)

ABSTRACT

The Gibbs energies of formation of MPt$_5$ (M $\equiv$ Nd, Dy, Ho, Er) intermetallic compounds were determined in the temperature range 900–1100 K using the solid state cell

Ta, M + MF$_3$ | CaF$_2$ | MPt$_5$ + Pt + MF$_3$, Ta

For M $\equiv$ Sm, a mixture of Gd + GdF$_3$ was used as the reference electrode. In the case of Eu, a mixture of Eu + EuF$_2$ served as the reference electrode. The trifluorides of Sm and Eu are not stable in equilibrium with the metal. The fluoride phase coexisting with a SmPt$_5$ + Pt mixture is SmF$_3$, whereas EuF$_2$ is the equilibrium phase in contact with EuPt$_5$ + Pt. All the MPt$_5$ compounds studied (except EuPt$_5$) exhibit similar stability. Europium is divalent in the pure metal and trivalent in EuPt$_5$. The energy required for the promotion of divalent Eu to the trivalent state accounts for the less negative Gibbs energy of formation of EuPt$_5$. The enthalpies of formation of all the MPt$_5$ compounds obtained in this study are in good agreement with Miedema's model.

INTRODUCTION

The platinum-rich intermetallic compounds of rare earth elements are of interest from the practical as well as the theoretical point of view. It is known [1] that rare earth oxides can be reduced in the presence of platinum by dry hydrogen or ammonia at temperatures above 1473 K, resulting in the formation of MPt$_5$ compounds, where M represents a rare earth element. This indicates very high stability of the intermetallic phases. Based on the experimental observation of Bronger [1], Wengert and Spanoudis [2] have estimated the upper limit for the Gibbs energy of formation of some MPt$_5$ compounds. It is possible to recover some rare earth metals from the MPt$_5$ intermetallics by sublimation at elevated temperature. In order to compute

the optimum temperatures for the recovery of the rare earth metals, accurate thermodynamic data are required.

All the rare earth elements except Ce can be described by a localized 4f (core) electron model. The elements Eu and Yb are divalent in their elementary metallic state. These metals can be treated as having two conduction electrons per atom and M^{2+} ionic cores. The divalent state is preferred because of the stability associated with half-filled and filled 4f states. In intermetallic compounds, Eu and Yb may be present in the trivalent state if the energy required for promotion to the higher-valent state is recouped by the larger heat of formation of the intermetallic. Thus the energies of formation of intermetallics containing Eu and Yb can provide confirmation of the oxidation state and transformation energy.

Platinum forms a series of intermetallic compounds with each rare earth metal [3–5]. The compound with the highest concentration of Pt has the formula MPt_5 for M ranging from La to Tm. For Yb and Lu, the compound having the highest concentration of Pt is MPt_3, which has the Cu_3Au structure [1,3,4]. The MPt_5 compounds containing the lighter lanthanides crystallize in the hexagonal Cu_5Ca structure [1]. For $M \equiv Sm$, Eu and Gd the structure is similar, but the powder pattern contains more reflections. The structure has rhombic symmetry [1]. A further small change in structure occurs at Tb. The lanthanide contraction is manifested by the shrinkage in the a axis or the a and b axes, whereas the c axis becomes larger. The crystal structures of MPt_5 compounds containing heavier rare earth metals have not been fully elucidated.

Since the literature does not contain any report about thermodynamic measurements on MPt_5 compounds containing rare earths, solid state galvanic cell studies have been undertaken on systems containing Nd, Sm, Eu, Dy, Ho and Er in the temperature range 900–1100 K. For $M \equiv Nd$, Dy, Ho and Er, the galvanic cell had the configuration represented by

$$Ta, M + MF_3 \,|\, CaF_2 \,|\, MPt_5 + Pt + MF_3, Ta \qquad (I)$$
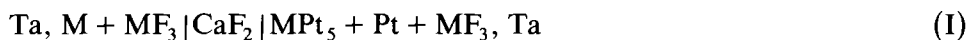
Single crystal CaF_2 was used as the solid electrolyte and Ta wire as the electrical lead to the electrodes. The EMF of cell (I) gives directly the Gibbs energy of formation of MPt_5 without the use of any auxiliary data. For $M \equiv Sm$ and Eu, Kim and Oishi [6] indicate that the difluoride rather than the trifluoride coexists with the metal. Accurate data on Gibbs energies of formation of the difluorides at high temperatures are not available. The equilibrium fluoride phase coexisting with the $SmPt_5 + Pt$ mixture is actually SmF_3. Because of the low activity of Sm, the higher fluoride is stabilized by virtue of the reaction

$$\langle MF_2 \rangle \rightarrow \tfrac{1}{3}\langle M \rangle + \tfrac{2}{3}\langle MF_3 \rangle \qquad (1)$$

where the angled brackets represent solids. However, the $EuPt_5 + Pt$ phase mixture is in equilibrium with EuF_2. EuF_2 is so much more stable than EuF_3

that, even at the low activity of Eu prevailing in a mixture of $EuPt_5$ and Pt, equilibrium is not shifted to the right. Hence the following cells were used for the measurement of the stability of $SmPt_5$ and $EuPt_5$

$$\text{Ta, Gd} + GdF_3 \,|\, CaF_2 \,|\, SmPt_5 + Pt + SmF_3, \text{Ta} \qquad \qquad \text{(II)}$$

$$\text{Ta, Eu} + EuF_2 \,|\, CaF_2 \,|\, EuPt_5 + Pt + EuF_2, \text{Ta} \qquad \qquad \text{(III)}$$

Auxiliary thermodynamic data on SmF_3 and GdF_3 are required for calculating the free energy of formation of $SmPt_5$ from the EMF of cell (II).

EXPERIMENTAL

Materials

The purity of the starting materials was 99.9% for the rare earth metals and 99.99% for Pt. The MPt_5 intermetallic compounds were prepared both by arc melting on a water cooled copper hearth and by solid state reaction of powders under prepurified argon. High purity argon was further dried over P_2O_5 and deoxygenated by passage through granules of Ti at 1173 K. The buttons of alloy were remelted two or three times to ensure homogeneity. Weight losses were found to be negligible. The final composition of the compounds was confirmed by chemical analysis. In the powder technique of 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 between 1125K and 1200 K. The reactions were exothermic. The intermetallic compounds were annealed under high vacuum at 1100 K for 300 ks. The formation of MPt_5 was confirmed by X-ray diffraction. Single crystals of CaF_2 of 99.999% purity were obtained from Harshaw Chemical Company. The rare earth fluorides used in the electrodes were of 99.9% purity.

Apparatus and procedure

The EMF of cells (I), (II) and (III) was measured as a function of temperature from 900–1100 K. The EMF response was very sluggish at temperatures below 900 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 1300 K. The reference electrode was prepared by compacting an intimate mixture of rare earth metal and its coexisting fluoride in the molar ratio 2:1 and sintering under prepurified flowing argon at 1300 K.
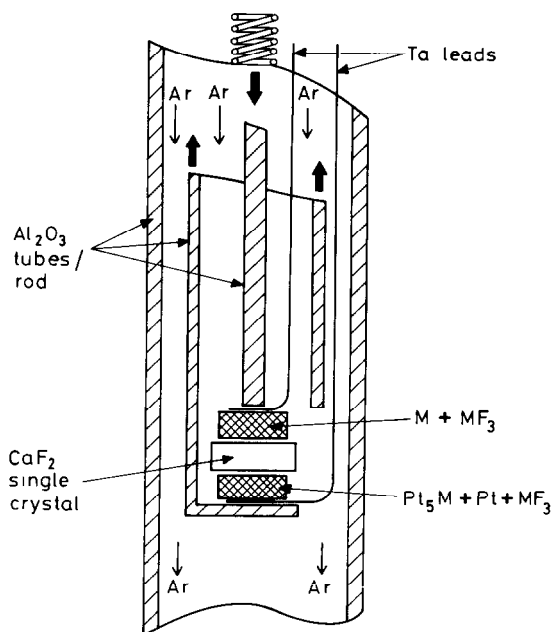
Fig. 1. Schematic diagram of the EMF apparatus.

A schematic diagram of the apparatus is shown in Fig. 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 foil were held together under pressure by 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 Fig. 1. 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 prepurified argon at a pressure of 1.02×10^5 Pa. The apparatus was evacuated and refilled with argon twice at room temperature and ca. 600 K. Internal getters of zirconium were placed adjacent to the electrodes to scavenge residual oxygen from the argon; mixed potentials arising from the oxidation of the rare earth metal at the electrodes by residual oxygen in the inert gas was encountered in preliminary studies conducted without the use of internal getters. Even though the inert gas was deoxygenated prior to 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 contamination. Flux of oxygen through the outer alumina tube because of the electrochemical permeability

of the ceramic was perhaps the second cause of contamination. Internal getters were effective in deoxygenating 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 ($> 10^{12}$ Ω) digital voltmeter. Cells (I) and (II) registered steady EMF values in 2 to 8 h after the attainment of thermal equilibrium, depending on the temperature of measurement. Cell (III) was more sluggish, requiring 4 to 12 h to attain a steady EMF.

The reversibility of the EMF was checked by passing small currents (ca. 40 μA) in either direction through the cell for ca. 300 s 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 2.5–6 ml s^{-1}. The EMF values of cells (I) and (II) were reproducible on temperature cycling to ± 1 mV. The EMF of cell (III) was reproducible to $\pm$ 2 mV. The temperature of the cell was measured by a Pt/Pt–13% Rh thermocouple and controlled to ± 1 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 the experiment.

RESULTS

The variation of the EMF of cell (I) with temperature is shown in Fig. 2 for M $\equiv$ Nd, Dy, Ho and Er. The temperature dependence of the EMF values of cells (II) and (III) are shown in Fig. 3. Within experimental error, the EMF is a linear function of temperature. Equations for the EMF, obtained by least-mean-square regression analysis of experimental data, are given in Table 1. The error limits correspond to twice the standard deviation.

Pure CaF$_2$ is predominantly a fluoride ion conductor over a wide range of fluorine partial pressure and temperature. At high temperature it begins to exhibit electronic conduction at fluorine potentials close to that corresponding to the decomposition of CaF$_2$ [7]. At the fluorine potentials established at the electrodes during this investigation, the average ionic transport number in CaF$_2$ is greater than 0.98. The EMF of the galvanic cell can therefore be related to the Gibbs energy change for the virtual cell reaction. For cells (I) and (III), the EMF gives directly the chemical potential of the rare earth elements (M) in the phase mixture MPt$_5$ + Pt

$$\Delta\mu_M = RT \ln a_M = -\eta FE \qquad (2)$$

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 (I) and 2
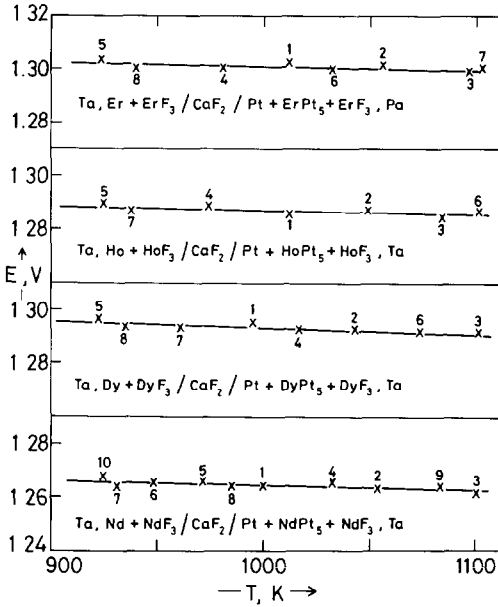
Fig. 2. Temperature dependence of the EMF of cell (I) for M ≡ Nd, Dy, Ho and Er.
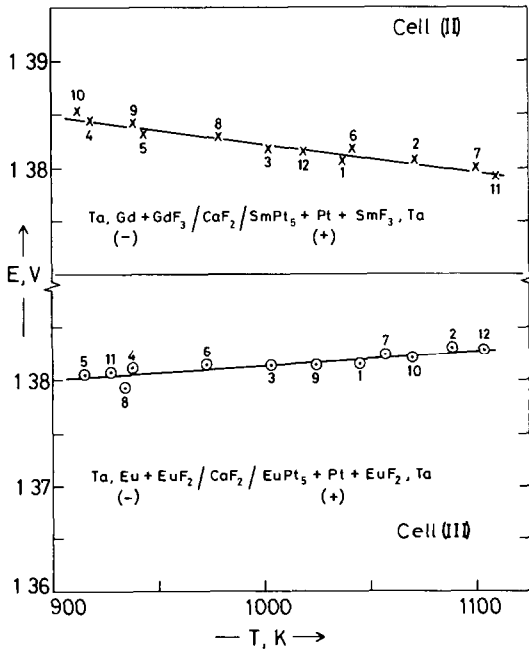

Fig. 3. Variation of the EMF of cells (II) and (III) with temperature.

TABLE 1

Expressions for the EMF of different cells and Gibbs energy of formation of MPt_5 phases

| Cell	EMF (mV)	$\Delta G_f^{\ominus} \langle MPt_5 \rangle$ (J mol^{-1})
Ta, Nd + NdF$_3$ | CaF$_2$ | NdPt$_5$ + Pt + NdF$_3$, Ta	$1283 - 0.019T$ (± 0.9)	$-371410 + 5.50T$ (± 500)
Ta, Dy + DyF$_3$ | CaF$_2$ | DyPt$_5$ + Pt + DyF$_3$, Ta	$1318 - 0.025T$ (± 1.1)	$-381540 + 7.24T$ (± 500)
Ta, Ho + HoF$_3$ | CaF$_2$ | HoPt$_5$ + Pt + HoF$_3$, Ta	$1302 - 0.015T$ (± 1.0)	$-376910 + 4.34T$ (± 500)
Ta, Er + ErF$_3$ | CaF$_2$ | ErPt$_5$ + Pt + ErF$_3$, Ta	$1317 - 0.016T$ (± 1.2)	$-381250 + 4.63T$ (± 500)
Ta, Gd + GdF$_3$ | CaF$_2$ | SmPt$_5$ + Pt + SmF$_3$, Ta	$1408 - 0.0255T$ (± 1.3)	$-375300 + 5.02T$ (± 600 [a])
Ta, Eu + EuF$_2$ | CaF$_2$ | EuPt$_5$ + Pt + EuF$_2$, Ta	$1368 + 0.0132T$ (± 2.5)	$-264050 - 2.55T$ (± 1200)

[a] If the uncertainty in auxiliary thermodynamic data on GdF$_3$ and SmF$_3$ are included, the error estimate is ± 15000 J mol^{-1}.

for cell (III). The standard Gibbs energy of formation of MPt_5 intermetallics is equal to the chemical potential of M in the two-phase mixture MPt_5 + Pt.

$$\langle M \rangle + 5 \langle Pt \rangle \rightarrow \langle MPt_5 \rangle \tag{3}$$

$$\Delta G_f^{\ominus} = \Delta \mu_M (MPt_5 + Pt) \tag{4}$$

The virtual cell reaction corresponding to cell (II) can be written as

$$\langle SmF_3 \rangle + 5 \langle Pt \rangle + \langle Gd \rangle \rightarrow \langle GdF_3 \rangle + \langle SmPt_5 \rangle \tag{5}$$
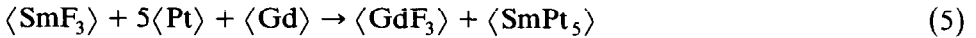
for which

$$\Delta G_R^{\ominus} = -3FE = \Delta G_f^{\ominus} \langle GdF_3 \rangle + \Delta G_f^{\ominus} \langle SmPt_5 \rangle - \Delta G_f^{\ominus} \langle SmF_3 \rangle \tag{6}$$

Using values for the Gibbs energy of formation of solid GdF$_3$ and SmF$_3$ from the compilation of Pankratz [8], the standard Gibbs energy of formation of SmPt$_5$ can be computed from the EMF data. The Gibbs energies of formation of all MPt_5 compounds obtained in this study are summarized in Table 1.

The Gibbs energy of formation of rare earth MPt_5 compounds at 1000 K is plotted in Fig. 4 as a function of atomic number. The data for GdPt$_5$ are from a recent EMF measurement [9]. It is seen that the Gibbs energy of formation of EuPt$_5$ is significantly more positive than those for the other rare earth MPt_5 compounds. Magnetic susceptibility and Mössbauer spectroscopic studies of de Graaf et al. [10] show that Eu is trivalent in EuPt$_5$ and becomes a mixed-valence species in the solid solution based on EuPt$_2$.
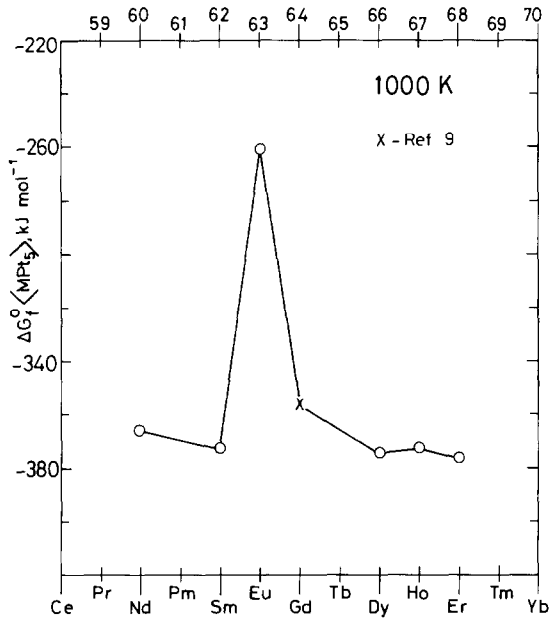
Fig. 4. Gibbs energy of formation of lanthanide MPt$_5$ compounds as a function of atomic number.

The lattice dimensions and close similarity of the compounds Eu$_5$Pt$_2$, Eu$_3$Pt$_2$ and Eu$_5$Pt$_4$ 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 metals rather than of the trivalent rare earth metals. The molar volume and magnetic behaviour of Eu are different from those expected for a trivalent rare earth metal. The energy difference between the trivalent and divalent modification of Eu has been discussed from an experimental point of view by Gschneidner [11] and by Bayanov and Afanas'ev [12]. 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 chloride 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 [11] obtained a value of 96.2 kJ g atom^{-1} as the average value of the energy difference between divalent and trivalent modifications of Eu. Bayanov and Afanas'ev suggest a value of 92 kJ g atom^{-1}. This energy required for the promotion of divalent Eu to the trivalent state accounts for the less negative Gibbs energy of formation of EuPt$_5$ compared with the other MPt$_5$ rare earth intermetallics.

DISCUSSION

The experimental data on enthalpy of mixing obtained in this study can be compared with the charge transfer model of Miedema and co-workers [13–15]. 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}).

$$\Delta H_f^{\ominus} = 2f(x)\left[(1-x)V_A^{2/3} + xV_B^{2/3}\right]\frac{-P(\Delta\phi')^2 + Q(\Delta n_{ws}^{1/3})^2}{(\eta_{ws}^A)^{-1/3} + (\eta_{ws}^B)^{-1/3}} \qquad (7)$$

where P and Q are constants of the model and

$$f(x) = C_A^S C_B^S\left[1 + 8(C_A^S C_B^S)^2\right] \qquad (8)$$

The surface area concentration of A is given by

$$C_A^S = (1-x)V_A^{2/3}\left[(1-x)V_A^{2/3} + xV_B^{2/3}\right]^{-1} \qquad (9)$$

For Eu, model parameters are given both for divalent and trivalent states [15]. Therefore the enthalpy of formation of $EuPt_5$ from both divalent Eu and hypothetical trivalent state can be computed using the model. The enthalpy of formation of $EuPt_5$, in which Eu exists in the divalent state from divalent Eu and Pt, is -243 kJ mol^{-1}. From hypothetical trivalent Eu and Pt, the enthalpy of formation of $EuPt_5$ containing trivalent Eu is -355 kJ mol^{-1}. Therefore the formation enthalpy of the actual $EuPt_5$ containing trivalent Eu from pure divalent Eu and Pt is -259 kJ mol^{-1}. The value of

TABLE 2

Comparison between the second-law enthalpy of formation of rare earth MPt_5 compounds and Miedema's model

Compound	Second law $\Delta H_f^0\langle MPt_5\rangle$ (kJ mol^{-1})	Miedema's model $\Delta H_f^0\langle MPt_5\rangle$ (kJ mol^{-1})
$NdPt_5$	-371.4 (± 4)	-353 (± 20)
$SmPt_5$	-375.3 (± 20)	-356 (± 20)
$EuPt_5$	-264.0 (± 8)	-243 (± 20) [a]
		-355 (± 20) [b]
		-259 (± 20) [c]
$DyPt_5$	-381.5 (± 4)	-353 (± 20)
$HoPt_5$	-376.9 (± 4)	-344 (± 20)
$ErPt_5$	-381.3 (± 4)	-354 (± 20)

[a] Formation of $EuPt_5$ containing divalent Eu from divalent Eu metal and Pt.
[b] Formation of $EuPt_5$ containing trivalent Eu from hypothetical trivalent Eu metal and Pt.
[c] Formation of $EuPt_5$ containing trivalent Eu from divalent Eu metal and Pt.

TABLE 3

Comparison between the Gibbs energies of formation of MPt_5 compounds obtained in this study and the limits suggested by Wengert and Spanoudis [2]

Compound	Temperature (K)	$\Delta G_f^0 \langle MPt_5 \rangle$ (kJ mol^{-1})	
		This study	Wengert and Spanoudis
$NdPt_5$	1473	-371.4	$-$
$SmPt_5$	1623	-367.1	< -246
$EuPt_5$	1623	-268.2	< -143
$DyPt_5$	1473	-370.9	< -294
$HoPt_5$	1473	-370.5	< -447
$ErPt_5$	1473	-374.4	< -316

Gschneidner [11] for the transformation energy of Eu is used in this calculation. The computed enthalpy compares well with the second-law value of -264 kJ mol^{-1} obtained from EMF data. The comparison of the enthalpies of formation of MPt_5 compounds obtained from Miedema's model and this study is provided in Table 2. It is seen that Miedema's model predicts the enthalpy of formation of MPt_5 compounds involving rare earth elements with useful accuracy. Small changes in the values for the model parameters ϕ' and η_{ws} can alter the predicted values significantly. The uncertainty in the model prediction is at least ± 20 kJ mol^{-1}.

The upper limits for the Gibbs energy of formation of MPt_5 compounds suggested by Wengert and Spanoudis [2], based on the experiments of Bronger [1], are listed in Table 3 in comparison with data obtained in this study. The estimated upper bounds are compatible with the direct experimental information except for $HoPt_5$.

The entropies of formation of MPt_5 compounds are negative except for Eu, varying from -4.3 J mol^{-1} K^{-1} to -7.2 J mol^{-1} K^{-1}. These small negative values are consistent with the large negative enthalpies of formation of MPt_5 compounds. The vibrational frequency of atoms in the intermetallic compound is probably higher than in the component solid metals. In the case of $EuPt_5$ the entropy of formation is 5 J mol^{-1} K^{-1}. A small positive contribution may arise from the transformation of divalent Eu in the pure metal to the trivalent state in $EuPt_5$. Because of the small values for the entropy of formation, the Gibbs energy of formation is only a weak function of temperature.

CONCLUSIONS

Direct experimental data on Gibbs energy of formation of six rare earth MPt_5 compounds have been generated using galvanic cells incorporating single crystal CaF_2 as the solid electrolyte. The enthalpy and entropy of

formation of MPt_5 intermetallics are derived from EMF data. The enthalpies of formation obtained from experimental data compare well with the predictions of Miedema's model [13–15]. The Gibbs energy and enthalpy of formation of the $EuPt_5$ compound are substantially less negative than values obtained for the other rare earth MPt_5 compounds. The energy required to promote divalent Eu to the trivalent state accounts for the lower stability of $EuPt_5$.

ACKNOWLEDGEMENTS

REFERENCES

1 W. Bronger, J. Less-Common Met., 12 (1967) 63.
2 P.R. Wengert and L. Spanoudis, J. Am. Ceram. Soc., 57 (1974) 94.
3 W.G. Moffatt (Ed.), Handbook of Binary Phase Diagrams, Business Growth Services, General Electric Co., Schenectady, NY, 1985.
4 T.B. Massalski (Ed.), Binary Alloy Phase Diagrams, Vols. 1 & 2, American Society for Metals, Metals Park, OH, 1986.
5 A. Iandelli and A. Palenzona, J. Less-Common Met., 80 (1981) 71.
6 Y.C. Kim and J. Oishi, J. Less-Common Met., 65 (1979) 199.
7 J. Delcet, R.H. Heus and J.J. Egan, J. Electrochem. Soc., 125 (1978) 755.
8 L.B. Pankratz, Thermodynamic Properties of Halides, Bull. U.S. Bur. Mines, No. 674, 1984.
9 K.T. Jacob and Y. Waseda, Mater. Trans. (JIM), 31 (1990) 135.
10 H. de Graaf, R.C. Thiel and K.H.J. Buschow, Physica B, 100 (1980) 81.
11 K.A. Gschneidner, J. Less-Common Met., 17 (1969) 1.
12 A.P. Bayanov and Yu. A. Afanas'ev, Russ. J. Phys. Chem., 47 (1973) 796.
13 A.R. Miedema, R. Boom and F.R. de Boer, J. Less-Common Met., 41 (1975) 283.
14 P.C.P. Bouten and A.R. Miedema, J. Less-Common Met., 71 (1980) 147.
15 A.K. Niessen, F.R. de Boer, R. Boom, P.F. de Châtel, W.C.M. Mattens and A.R. Miedema, CALPHAD, 7 (1983) 51.