Enthalpies of formation of Cd–Pr intermetallic compounds and thermodynamic assessment of the Cd–Pr system

Thomas L. Reichmann a,*, Klaus W. Richter a, Simona Delsante b, Gabriella Borzone b, Herbert Ipser a

a Department of Inorganic Chemistry (Materials Chemistry), University of Vienna, 1090 Wien, Austria
b Dipartimento di Chimica e Chimica Industriale, Università di Genova, 16146 Genova, Italy

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ABSTRACT

In the present study standard enthalpies of formation were measured by reaction and solution calorimetry at stoichiometric compositions of Cd6Pr, Cd3Pr, Cd58Pr13 and Cd6Pr. The corresponding values were determined to be $-46.0$, $-38.8$, $-35.2$ and $-24.7 \text{kJ/mol(at)}$, respectively. These data together with thermodynamic data and phase diagram information from literature served as input data for a CALPHAD-type optimization of the Cd–Pr phase diagram. The complete composition range could be described precisely with the present models, both with respect to phase equilibria as well as to thermodynamic input data. The thermodynamic parameters of all intermetallic compounds were modelled following Neumann–Kopp rule. Temperature dependent contributions to the individual Gibbs energies were used for all compounds. Extended solid solubilities are well described for the low- and high-temperature modifications of Pr and also for the intermetallic compound CdPr. A quite good agreement with all viable data available from literature was found and is presented.

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1. Introduction

In the last decades, the question of how to satisfy the ever increasing demand of energy has become most pressing for countries with high economic growth. The utilization of nuclear energy is sometimes inevitable for nations belonging to the group of developing and emerging countries. For an efficient use of nuclear energy, these countries have to establish strategies comprising an optimized reprocessing routine of spent nuclear fuels as well as an adequate waste management on the back-end of their nuclear fuel cycle. Indeed, low-level and intermediate-level radioactive waste is currently stored in interim storage facilities or deposited in geological repositories. Solutions for high-level waste are currently still in a planning stage and thus this type of waste is actually stored on-site.

Focusing onto reprocessing of nuclear waste, this is currently practiced by means of solvent extraction of actinides using tributyl phosphate (TBP), known as hydro-metallurgical technique or aqueous reprocessing (e.g., PUREX), respectively. Unfortunately, this technique deals with several problems like radiation and temperature instability of the various solvents used in the process. In addition, a huge amount of liquid waste is produced when applying PUREX or related processes. It is therefore reasonable to investigate an alternative type of reprocessing, called the pyrometallurgical technique. The latter technique is not dealing with the major disadvantages of the aqueous methods, as outlined by Olander [1], and it is described repeatedly in literature, see e.g., Refs. [2–5].

In particular, electro-transport and reductive extraction is applied to separate actinides and lanthanides from high-level radioactive waste inside an “electro-transporter” cell. The respective electro-chemical vessel contains a liquid metal pool at the bottom, covered by a molten salt solution serving as electrolyte. One basket anode, containing chopped nuclear fuels, and at least two cathodes are inserted into the liquid salt. During the process especially uranium, plutonium and minor actinides are transported whereas rare earth elements, alkaline and alkaline earth elements remain in the liquid salt. Additional reductive agents like Li are added to the salt which promotes the extractability of rare earth (RE) elements into the liquid metal pool at the bottom by forming intermetallic compounds. Moriyama et al. [6–7] determined that the separation factors, which are an indicator for extractability, are quite different between actinides and lanthanides. In principle, actinides have the higher affinity for extraction into a metal phase, a fact that is desirable, considering the chemical similarity to lanthanides. The extraction behaviour of different elements between a molten chloride salt phase and a liquid metal strongly depends on the standard free energy of formation of the corresponding chlorides as well as on the activity coefficients of the extracted elements in the
2. Literature overview

The Cd–Pr phase diagram has been investigated in detail by Reichmann et al. [11] who applied conventional methods, i.e. powder X-ray diffraction (XRD), differential thermal analysis (DTA), and scanning electron microscopy (SEM), to clarify the phase relationships, including extent of solid solutions, homogeneity ranges and isothermal reaction temperatures in the whole composition range. In addition, a complete literature survey concerning the intermetallic compounds observed within this system was given there. All intermetallic compounds, i.e. CdPr, Cd2Pr, Cd3Pr, Cd58Pr13, Cd6Pr and Cd11Pr, presented previously by Gschneidner and Calderwood [12], were confirmed. Additionally, an extended solid solubility of 22.1 at% Cd in the high-temperature allotropic modification of Pr was reported. Apparently, the addition of Cd stabilizes the high-temperature Pr modification obviously to the eutectoid decomposition reaction of Pr. Thus the separation factors are strongly influenced by the employed liquid metal which is preferentially Cd [8]. Therefore, a detailed knowledge of the respective Cd–Pr phase diagrams as well as of the thermodynamic stabilities of the corresponding intermetallic compounds is of great importance. This was the reason for initiating a series of thermodynamic and phase diagram studies of different Cd–Pr systems (cf. Refs. [9–11]).

It was the aim of the present study to perform a CALPHAD-type optimization of the complete Cd–Pr system based on relevant literature data on phase equilibria and thermodynamic properties, and supported by additional experimental values for the enthalpy of formation of the intermetallic compounds Cd2Pr, Cd3Pr, Cd58Pr13 and Cd6Pr.

| Reaction | \( T \) (°C) | Phase compositions (at% Cd) | Reaction type |
|----------|--------------|-----------------------------|--------------|
| \( L + \text{Cd}_{6}\Pr \rightleftharpoons \text{Cd}_{11}\Pr \) | 321 | \( \sim 100 \) | Degenerate peritectic |
| \( L + \text{Cd}_{6}\Pr \rightleftharpoons \text{Cd}_{11}\Pr + \text{L} \) | 570 | 97.2 | Peritectic |
| \( L + \text{Cd}_{6}\Pr \rightleftharpoons \text{Cd}_{11}\Pr \) | 734 | 92.4 | Peritectic |
| \( L + \text{Cd}_{6}\Pr \rightleftharpoons \text{Cd}_{11}\Pr \) | 875 | 87.0 | Congruent melting |
| \( \text{Cd}_{6}\Pr + \text{Cd}_{11}\Pr \rightleftharpoons \text{Cd}_{17}\Pr \) | 800 | 81.7 | Peritectic |
| \( \text{L} + \text{Cd}_{6}\Pr + \text{Cd}_{11}\Pr \rightleftharpoons \text{Cd}_{17}\Pr \) | 867 | 78.8 | Eutectic |
| \( \text{L} + \text{Cd}_{6}\Pr + \text{Cd}_{11}\Pr \) | 984 | 68.7 | Congruent melting |
| \( \text{L} + \text{Cd}_{6}\Pr + \text{Cd}_{11}\Pr \) | 869 | 78.8 | Peritectic |
| \( \text{L} + \text{Cd}_{6}\Pr + \text{Cd}_{11}\Pr \) | 999 | 50.0 | Congruent melting |
| \( \text{L} + \text{Cd}_{6}\Pr + \text{Cd}_{11}\Pr \) | 947 | 59.2 | Eutectic |
| \( \text{L} + \text{Cd}_{6}\Pr + \text{Cd}_{11}\Pr \) | 712 | 23.0 | Eutectic |
| \( \beta + \text{Pr} \rightleftharpoons \text{Cd}_{6}\Pr + \alpha + \text{Pr} \) | 437 | 17.0 | Eutectic |

* Reaction was modelled as degenerate eutectic \( \text{L} + \text{Cd} + \text{Cd}_{11}\Pr \) [compare text].
3. Experimental

To provide additional input data for the present CALPHAD-type optimization, calorimetric measurements were performed in two ways. Reaction calorimetric measurements were carried out in Genova to determine the enthalpy of formation of the intermetallic compound Cd$_{58}$Pr$_{13}$. In addition, solution calorimetry was used in Vienna to obtain enthalpies of formation of Cd$_2$Pr, Cd$_3$Pr, Cd$_{58}$Pr$_{13}$ and Cd$_6$Pr. The experimental setups of both methods are discussed in detail in Sections 3.1 and 3.2. All calorimetric results are listed in Table 2.

### 3.1. Reaction calorimetry

High purity Cd rods (5N, Koch-Light Laboratories LTD., Colnbrook, England) and Pr pieces (99.9%, Smart Elements, Vienna, Austria) were used for sample preparation. To lower diffusion paths and increase the reaction rate during the calorimetric synthesis, samples were prepared with Cd and Pr powders. The metals were filed inside a glove box under Ar atmosphere (oxygen level: $< 1$ ppm, water level: $< 1$ ppm) to prevent oxidation. The metal powders were then weighed according to calculated amounts, mixed homogeneously and pressed into compact pellets. For the calorimetric measurements, the pellets were enclosed in tight-sealed Ta crucibles to prevent oxidation and to avoid possible weight-losses due to the rather high vapour pressure of Cd. All calorimetric experiments were performed using a high precision Calvet-type twin calorimeter with two thermopiles with more than 200 thermocouples each. Enthalpies of formation were measured indirectly by dropping pure Cd (99.9999% Alfa Aesar, Karlsruhe, Germany), Pr (99.9%, Smart Elements, Vienna, Austria) and corresponding pieces of the intermetallic compounds into molten Sn at 823 °C. The intermetallic compounds were synthesized in their stoichiometric ratios using an isothermal isopiestic method according to Ref. [10]. All samples were determined to be pure single-phase by powder-XRD. An automated drop device was used and drops were performed under an Ar atmosphere. Ten sample pieces (between 30 and 50 mg each) and additional five pieces of NIST standard sapphire, for the calibration of the heat signal, were dropped at each calorimetric run. Graphite was used as crucible material. No reaction between the metals and the crucible material was observed in any measurement. Limiting heats of solution $\Delta_{sol}H_i^T$ were derived by extrapolation for Cd, Pr and the respective compounds and enthalpies of formation were evaluated according to

$$\Delta_{i}H_{Cd,Pr}^{(T)} = x\Delta_{sol}H_{Cd}^{(T)} + y\Delta_{sol}H_{Pr}^{(T)} - \Delta_{sol}H_{Cd,Pr}^{(T)}$$

where $T_d$ is the drop temperature (298 K). The furnace temperature and the drop temperature were recorded for each drop; the calculations were made using mean values over all drops. The scattering of the temperature signals were low and did not influence the measurements significantly.

Besides all instrumental errors, systematic errors were estimated to be mainly due to incomplete mixing of the samples with the solvent as well as due to evaporation of Cd. In general it was observed that some Cd condensed at the colder part of the silica glass tubes during the calorimetric runs. Therefore, the intervals between individual drops were reduced to 40 min. Although the effect was still present it was clearly less significant. According to the evaluation of the results of these measurements (compare chapter 4), the overall error for the enthalpies of formation is estimated to be $\pm 2$ kJ/mol(at).

### 3.2. Solution calorimetry

Solution calorimetry in liquid Sn was performed using a Calvet-type twin calorimeter with two thermocouples with more than 200 thermocouples each. Enthalpies of formation were measured indirectly by dropping pure Cd (99.9999% Alfa Aesar, Karlsruhe, Germany), Pr (99.9%, Smart Elements, Vienna, Austria) and corresponding pieces of the intermetallic compounds into molten Sn at 823 °C. The intermetallic compounds were synthesized in their stoichiometric ratios using an isothermal isopiestic method according to Ref. [10]. All samples were determined to be pure single-phase by powder-XRD. An automated drop device was used and drops were performed under an Ar atmosphere. Ten sample pieces (between 30 and 50 mg each) and additional five pieces of NIST standard sapphire, for the calibration of the heat signal, were dropped at each calorimetric run. Graphite was used as crucible material. No reaction between the metals and the crucible material was observed in any measurement. Limiting heats of solution $\Delta_{sol}H_i^T$ were derived by extrapolation for Cd, Pr and the respective compounds and enthalpies of formation were evaluated according to

$$\Delta_{i}H_{Cd,Pr}^{(T)} = x\Delta_{sol}H_{Cd}^{(T)} + y\Delta_{sol}H_{Pr}^{(T)} - \Delta_{sol}H_{Cd,Pr}^{(T)}$$

where $T_d$ is the drop temperature (298 K). The furnace temperature and the drop temperature were recorded for each drop; the calculations were made using mean values over all drops. The scattering of the temperature signals were low and did not influence the measurements significantly.

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The accuracy of the measurement and the evaluation of the error are discussed in detail in Refs. [18–20].

| Phase          | Solution calorimetry $\Delta_{sol}H_{i}^T$ [kJ mol$^{-1}$] | Reaction calorimetry $\Delta_{i}H_{i}^{T}$ [kJ mol$^{-1}$] |
|----------------|----------------------------------------------------------|----------------------------------------------------------|
| Cd$_2$Pr       | -24.7                                                   | -                                                       |
| Cd$_{58}$Pr$_{13}$ | -34.3*                                                 | -36.0*                                                 |
| Cd$_3$Pr       | -38.8                                                   | -                                                       |
| Cd$_6$Pr       | -46.0                                                   | -                                                       |

* Average of two measured values, see Section 3.

### 4. Thermodynamic modelling

The aim of the present work was to derive a set of thermodynamic model parameters, describing Gibbs energies of all phases in the system, which can be used as input data for a CALPHAD-type calculation. The optimization, described in detail by Lukas et al. [21], is based on obtaining the minimum total Gibbs energy of the system at constant temperature and pressure, yielding the composition and the amount of phases in equilibrium. For the calculations themselves the ThermoCalc® Classic software package (version S) [25] was used.

#### 4.1. Pure elements

The Gibbs energy function $0_{i}G^o_{i} = G^o_{i} - H^o_{i,SER}$ for element $i$ ($i=Cd$, Pr) in the phase $\theta$ ($\theta=\alpha-Pr$, $\beta-Pr$, Cd, or liquid) is described by a power series as defined by Dinsdale [26]. The corresponding parameters were taken from the SGTE 5.1 database included in the software package.

#### Table 2

Standard enthalpies of formation measured by reaction and solution calorimetry; estimated error $\pm 2$ kJ/mol(at); reference state: Cd(s), Pr(s).

| Phase          | Solution calorimetry $\Delta_{sol}H_{i}^T$ [kJ mol$^{-1}$] | Reaction calorimetry $\Delta_{i}H_{i}^{T}$ [kJ mol$^{-1}$] |
|----------------|----------------------------------------------------------|----------------------------------------------------------|
| Cd$_2$Pr       | -24.7                                                   | -                                                       |
| Cd$_{58}$Pr$_{13}$ | -34.3*                                                 | -36.0*                                                 |
| Cd$_3$Pr       | -38.8                                                   | -                                                       |
| Cd$_6$Pr       | -46.0                                                   | -                                                       |
4.2. Modelling of liquid and solid solution phases

The solid solutions based on α-Pr and β-Pr as well as the liquid phase were modelled in terms of a standard substitutional model with one sublattice. The molar Gibbs energy of a solution phase \( \theta \) is described as follows:

\[
G_m^\theta = G_{\text{ref}}^\theta + G_{\text{bd}}^\theta + G_{\text{int}}^\theta + G_{\text{other}} + \ldots
\]

where \( G_{\text{ref}}^\theta \) is the molar Gibbs energy of the weighted sum of the system constituents \( i \) in the crystallographic structure corresponding to the phase \( \theta \) relative to the chosen reference state (typically the stable element reference state, SER)

\[
G_{\text{ref}}^\theta = \sum_{i=1}^{n} x_i^\theta G_i^\theta
\]

and its temperature dependence is given by

\[
G(T) = a + bT + cT \ln(T) + \sum_n d_n T^n
\]

where \( a-d_i \) are adjustable coefficients.

The contribution to the Gibbs energy from ideal random mixing of the constituents in the crystal lattice or in the liquid, denoted \( G_{\text{bd}}^\theta \), is described as follows:

\[
G_{\text{bd}}^\theta = RT \sum_{i=1}^{n} x_i \ln(x_i)
\]

for a system consisting of \( n \) components.

The Gibbs energy which describes the effect of non-ideal mixing behaviour on the thermodynamic properties of a solution phase is given by the usual Redlich–Kister formalism [22]

\[
G_{\text{int}}^\theta = x_i \xi_j \left( L_i \xi_j + L_j \xi_i + 2 L_i L_j \xi_i \xi_j \right)
\]

where the temperature-dependent interaction parameters, describing the mutual interaction between constituents \( i \) and \( j \), are denoted \( \xi \). The temperature dependence of the interaction parameters is usually defined as

\[
\xi = \xi_0 + \xi_1 T
\]

4.3. Modelling of intermetallic phases

The intermetallic phase CdPr with CsCl-(B2-) structure was modelled with a two-sublattice model \((\text{Pr}_x\text{Cd}_{1-x})_{\text{B2}}\); since the experimental results indicate a homogeneity range to the Pr-rich side only, it was assumed that the Pr-sublattice remains fully occupied whereas on the Cd-sublattice a small amount of Cd-atoms can be substituted by Pr-atoms. This was discussed in detail in Ref. [11]. The \( G_{\text{ref}} \) for such a model is given by

\[
G_{\text{ref}}^\theta = \sum_i y_i x_j \xi_{ij} G_{ij}
\]

where the \( y \) terms are the site fractions of each constituent in the relevant sublattices, 1 and 2. The term \( G_{ij} \) is the Gibbs energy of formation of the “virtual compound” (or “end member”) \( ij \).

All other phases were treated as stoichiometric compounds, i.e. no variability concerning the composition was considered. The Gibbs energy is modelled relative to the surface of reference

\[
G_m^\theta = \sum_{i=1}^{n} b_i G_i^\text{SER}
\]

with \( G_i^\text{SER} \) as the Gibbs energy of component \( i \) in the stable element form and \( b_i \) as the stoichiometric coefficient for \( i \) in the phase \( \theta \).
from the present study were used as input values. The phase diagram was optimized according to the experimentally determined version published by Reichmann et al. [11] and thermodynamic parameters are listed in Table 3. Experimental Gibbs energies of formation at 823 K served as starting points for the modelling and the parameters for all stoichiometric phases were subsequently optimized according to experimental thermodynamic data. Since no thermodynamic information was available for the liquid, the parameters for the liquid were apparently around 3 at% Pr by substituting Cd sites. The corresponding model parameters are given in Table 3.

A temperature dependent phase transformation of Cd₃Pr, suggested in Ref. [11], was not considered in the calculations but from the present study. A comparison between calculated and experimentally determined invariant reaction temperatures is listed in Table 1. The entire composition range could be well described with the present model. Considering the rather small homogeneity ranges of the compounds (compare Refs. [10,11]) only CdPr was introduced with some solubility into the model while all other compounds were treated as line compounds. According to the results by Reichmann et al. [11], Cd₃Pr dissolves apparently around 3 at% Pr by substituting Cd sites. The corresponding model parameters are given in Table 3.

All line-compounds were modelled using temperature dependent contributions to the total Gibbs energies. The respective thermodynamic parameters are listed in Table 3. Experimental Gibbs energies of formation at 823 K served as starting points for the modelling and the parameters a and b for all stoichiometric phases were subsequently optimized according to experimental thermodynamic data. Since no thermodynamic information was available for the liquid, the parameters for the liquid were subsequently adapted to reproduce the experimental phase diagram data. Calculated Gibbs energies of formation at 823 K are shown together with values from literature in Fig. 3; it can be seen that the overall agreement is quite good. Similar as for the Gibbs energies of formation, it was possible to adjust Cd activities to the values determined experimentally by Reichmann and Ipser [10]. Again, the comparison presented in Fig. 4 shows very good agreement. Nevertheless, some deviations between calculated and experimentally determined Cd activities occurred in the two-phase fields adjacent to Cd₃₃Pr₁₁. Considering that the stochiometric compositions of Cd₃₃Pr₁₁ and Cd₈₈Pr₁₃ are very close to each other, it was reasonable to model them with a similar temperature dependence of the energy contribution. Only in this way it was possible to model both compounds stable in the whole temperature range.

**Table 3**

| Compound | Gibbs Energy of Formation (kJ/mol) |
|----------|-----------------------------------|
| Cd₆Pr    | GHSERCD + 0.857 GHSERPR - 26502.7 + 6.6T |
| Cd₃₃Pr₁₁ | GHSERCD + 0.817 GHSERPR - 33664.4 + 9.5T |
| Cd₈₈Pr₁₃ | GHSERCD + 0.804 GHSERPR - 34708.7 + 10.12T |
| Cd₄Pr    | GHSERCD + 0.75 GHSERPR - 39827.2 + 12.3T |
| Cd₃Pr    | GHSERCD + 0.667 GHSERPR - 45989.7 + 14.2T |
| Cd₂Pr    | GHSERCD + 0.5 GHSERPR - 47613.2 + 15.7T |
| CdPr     | GHSERCD + 0.483 GHSERPR - 61805.5 + 3T |

**Fig. 2.** Comparison of the calculated Cd–Pr phase diagram with data available from literature; open triangles and circles: DTA values, plus signs: SEM data, both from Reichmann et al. [11]; filled triangles: Johnson et al. [13].
temperature range. The values shown in Fig. 4 lead to the best consistency of all input data.

As described above, the modelled Gibbs energies of formation for Cd₆Pr, Cd₅₈Pr₁₃, Cd₃Pr and Cd₂Pr are based on the enthalpy values from the present calorimetric measurements, compare Table 2. The respective calculated enthalpies of formation were compared with those determined experimentally (Fig. 1). Considering the accuracy of ±2 kJ/mol(at) of the calorimetric measurements, the respective calculated enthalpies of formation are within the error limit.

As can be observed in Table 3, only the parameters a and b were modelled for the individual Gibbs energies of the intermetallic compounds, following the Neumann–Kopp rule. Cₚ data of Cd₁₁Pr were measured by DSC by Kumar et al. [24] between 300 and 550 K. The comparison with the calculated values, shown in Fig. 5, indicates that the deviation of the heat capacity of Cd₁₁Pr from Neumann–Kopp’s rule is minimal (within the experimental error) and does not require the introduction of higher order terms to the Gibbs energy description.

The intermetallic compound CdPr was modelled with an ideal two-sublattice model. By modelling of the hypothetical end member ⁰GᵦPr, using a temperature dependent contribution, the homogeneity range of CdPr was optimized according to the experimental data.

The solid solutions of Cd in the low- (DHCP, α-Pr) and high-temperature (BCC, β-Pr) modifications of Pr were modelled according to the Redlich–Kister formalism using one (⁰L) and two (⁰L, ¹L) interaction parameters, respectively. In order to describe the experimentally determined liquidus along the whole composition range with the present model, three interaction parameters ⁰L, ¹L and ²L were required for the liquid phase.

It should be pointed out that the present thermodynamic optimization is exclusively valid for the temperature range between 298 and 3200 K and does not include temperatures above and below.

6. Summary

Standard enthalpies of formation of the four intermetallic compounds Cd₆Pr, Cd₅₈Pr₁₃, Cd₃Pr and Cd₂Pr were measured by calorimetry. Solution calorimetry was employed for all four compounds and the enthalpy of formation of stoichiometric Cd₅₈Pr₁₃ was also measured by direct reaction calorimetry. The experimental values for Cd₅₈Pr₁₃ from the two different methods were in good agreement with each other, and an average value of −35 ± 2 kJ/mol(at) is suggested. All present calorimetric data together with thermodynamic data from literature served as input data for a thermodynamic assessment of the Cd–Pr phase diagram. The complete composition range including all invariant reactions could be calculated, and the agreement with phase diagram data presented by Refs. [11,13] is very good. A comparison of calculated and experimentally determined phase diagram is given in Fig. 2 and Table 1. A temperature dependent contribution to the individual Gibbs energy was introduced for all phases to guarantee a consistent description of all input data.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.calphad.2014.06.005.

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