

Thermochemistry of the rare earth alloys with the 14th group elements

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Abstract: Interest in the crystallochemistry, physical properties and stability of intermetallic compounds is increasing, especially with regard to their potential applications in electronic and magnetic devices. Particular attention has been devoted to the rare earth (R) alloys. The results recently obtained in our laboratories in the thermodynamic investigation of several R-X (X = Sn, Pb) alloys are discussed with reference to the thermochemical properties of those formed with the elements of the 14th group of the Periodic Table. A few recent results obtained for some X-rich alloys are also given.

INTRODUCTION

The rare earths (R) are highly electropositive and reactive metals that include (1) Sc, Y and the Lanthanides, which constitute a inner periodicity interval within the transition metal group. These elements can be divided into "light earths" (those between La and Eu) and "heavy earths" (those between Gd and Lu). Yttrium, owing to its small atomic volume, is often associated with the heavy earths: its metallic radius value falls between those of Dy and Ho. The data for Sc can be compared to those of the Lanthanides, but generally a clearly different behaviour can be noted.

Systematic investigation of the compounds formed in the binary rare earth systems reveals a distinct trend for the alloys formed with one of the elements in the *p-block* of the Periodic Table. A steady decrease in intermetallic properties is observed on passing from one group to the next and may be related to a continuous change in the constitutional properties (shape of the phase diagram, melting temperature, enthalpies of formation, etc.). This trend is particularly evident for alloys formed with the 14th elements. Covalent combinations (possibly with a certain degree of ionic bonding) are mainly formed with C, Si and Ge, whereas Sn and Pb usually give rise to intermetallic phases.

The alloying behaviour of the rare earths with these five elements in some selected cases is briefly described in this paper. Particular attention is devoted to the thermochemical features of these alloys. Results obtained in the authors' laboratories in thermodynamic studies of several R-Sn and R-Pb alloys are also reported in summary form. Moreover, recent results obtained in the investigation of some X-rich R-X alloys will be presented. It will also be shown that the data for some Nd-Sn, Sm-Pb and Gd-Pb alloys fit the general trends already observed.

R-X ALLOYS (X = C, Si, Ge, Sn, Pb): SYSTEMATICS AND CONSTITUTIONAL PROPERTIES

Not all the possible R-X combinations have been completely studied. Data concerning the R-C binary systems have been assessed by K.A. Gschneidner Jr. (2) and by G. Adachi *et al.* (3), while for R-Si and R-Ge alloys, a critical evaluation of the data can be found in A.B. Gokhale *et al.* (4, 5). Data on phase diagrams and structural properties have been summarized for a few R-Sn [R= La (6), Gd (7), Yb (8)] and R-Pb systems [R= La (9), Gd (10), Yb (11)]. The R-Pb alloys, are reviewed by K.A. Gschneidner Jr. (12). Information on several thermodynamic properties has also been given in all these papers.

Fig. 1 shows typical aspects of the well-known phase diagrams formed by Pr with the 14th group elements. The reassessed version of the Nd-Sn diagram (14) has also been included to reflect the changes should be made in the Pr-Sn phase diagram according to the results of recent (mainly crystallographic) investigations (16). According to the general alloying behaviour of Pr and Nd, the corrected version of the Pr-Sn should be similar to the Nd-Sn phase diagram here reported.

Fig. 2 illustrates the progressive change that occurs when different R are alloyed with the same X metal (Pb in this case). Trends of this kind and their correlations with several properties such as, atomic radius, electronegativity, etc., may also be useful as a specific criterion for evaluating measurement reliability and predicting missing data by interpolation. For a discussion of the general aspects of this subject, see for instance (12, 17-19) on their possible application to phase equilibria prediction and on the estimation of crystallochemical and thermodynamic properties. For typical trends observed in the investigation of selected groups of R alloys and compounds with the same partner, see (12, 20).

FORMATION THERMOCHEMISTRY OF THE BINARY RARE EARTH COMPOUNDS WITH C, Si, Ge, Sn AND Pb

The properties of the compounds formed by the 14th group elements, have resulted in the need to adopt a variety of experimental methods and techniques. In many cases, emf and vapour pressure methods have been used, so that the $\Delta_f H$ has been indirectly obtained by computation. Recently, however, more reliable $\Delta_f H$ data have been provided by calorimetry. A short summary on this point is given below.

Solution calorimetry: the heat of formation is obtained as the difference between the heats of solution, measured in a high temperature calorimeter, of the component elements and of the compound respectively. The solvent consists of a suitable metallic bath (molten Sn, Al, etc.). *Direct calorimetry*: the alloy is synthesized by heating a compact of the component powders in the calorimeter itself and measuring the heat generated. *Drop calorimetry*: in which the compact is dropped from room temperature into a high temperature calorimeter, can be considered a variation of the direct calorimetric methods. *Dynamic differential calorimetry (DDC)*: is a kind of quantitative differential thermal analysis carried out on samples in which transformations or reactions occur. Several reviews on these topics in the particular field of alloy thermochemistry have been published in recent years (21-28).

Considering now the specific behaviour of the R-X alloys, the following points may be mentioned (all the data are referred to moles of atoms: for instance 1/3 (LaSi₂), 1/4 (LaPb₃), etc.).

1. Carbides Measurements were mainly carried out in the past with: emf at high temperature (29), combustion calorimetry (30) and vaporization studies (mass spectrometry Knudsen effusion method) (31, 32) to determine the thermodynamic properties of solid R carbides. In vaporization studies, reduction of high-temperature vapour pressure data to $\Delta_f H$ at room temperature is often problematic.

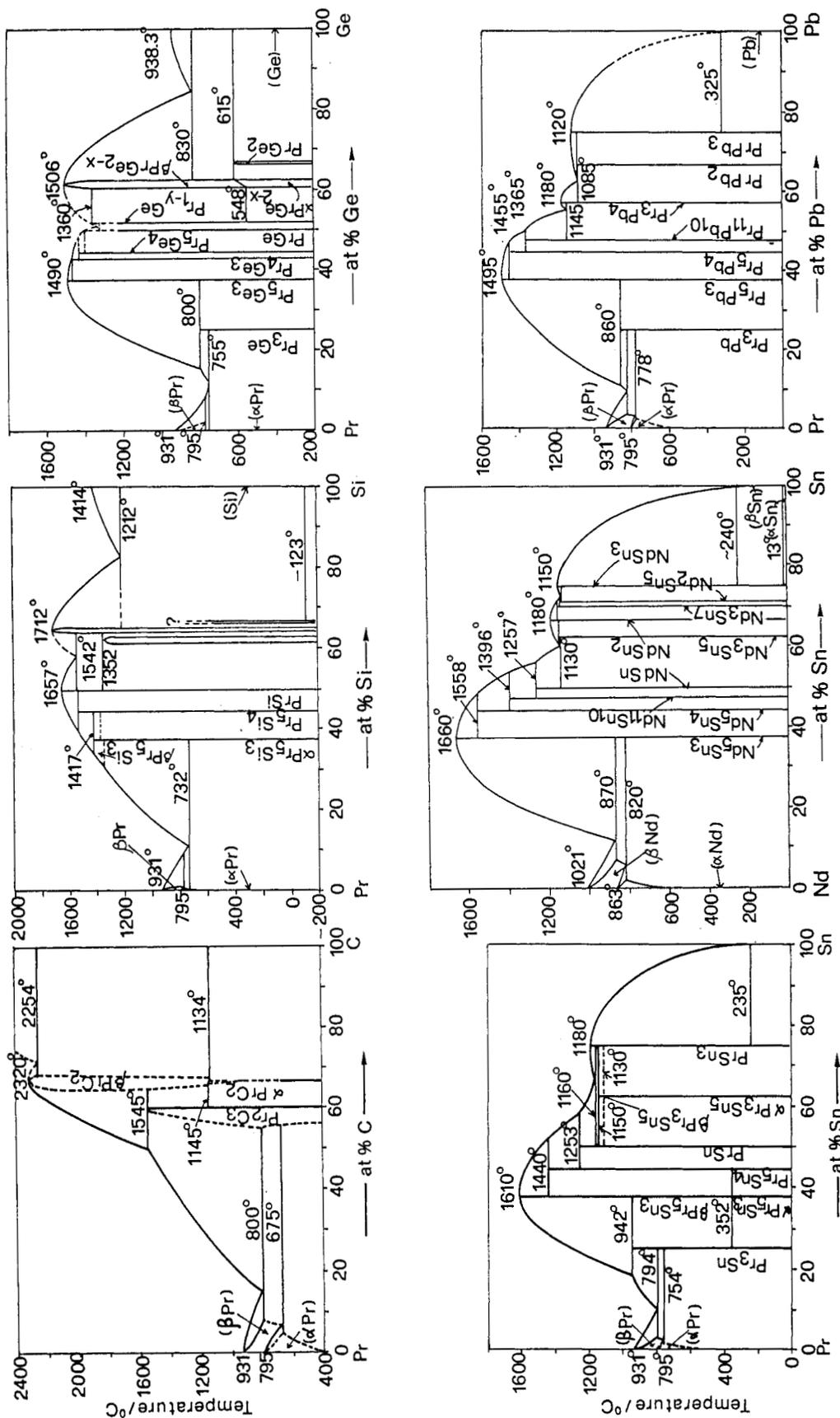


Fig. 1 Typical R-X phase diagrams. Systems of Pr with the elements of the 14th group, drawn according to Massalski (13) and of Nd with Sn (14). For Pr-Si, a few modifications have been introduced as suggested by (15); note the three phases with compositions close to PrSi₂.

Ce, Pr, Nd, Gd and Lu have been investigated. A few selected values are presented in Fig. 3. Wide scattering of the data is evident, especially for the R-rich alloys and for the data derived from emf measurements. In this case, only an average trend for the light earths may be given. The great disparity of the emf data reflects the difficulties often met when trying to obtain accurate enthalpies of formation values from indirect measurements.

3. Germanides High temperature emf methods (35) have been systematically used, as well as drop calorimetry in high temperature solvents (liquid Ni-Ge alloys) (39) and high temperature direct synthesis calorimetry (34).

Germanides of Sc, Y, La, Ce, Pr, Nd and Gd were studied. Typical results are presented in Fig. 3.

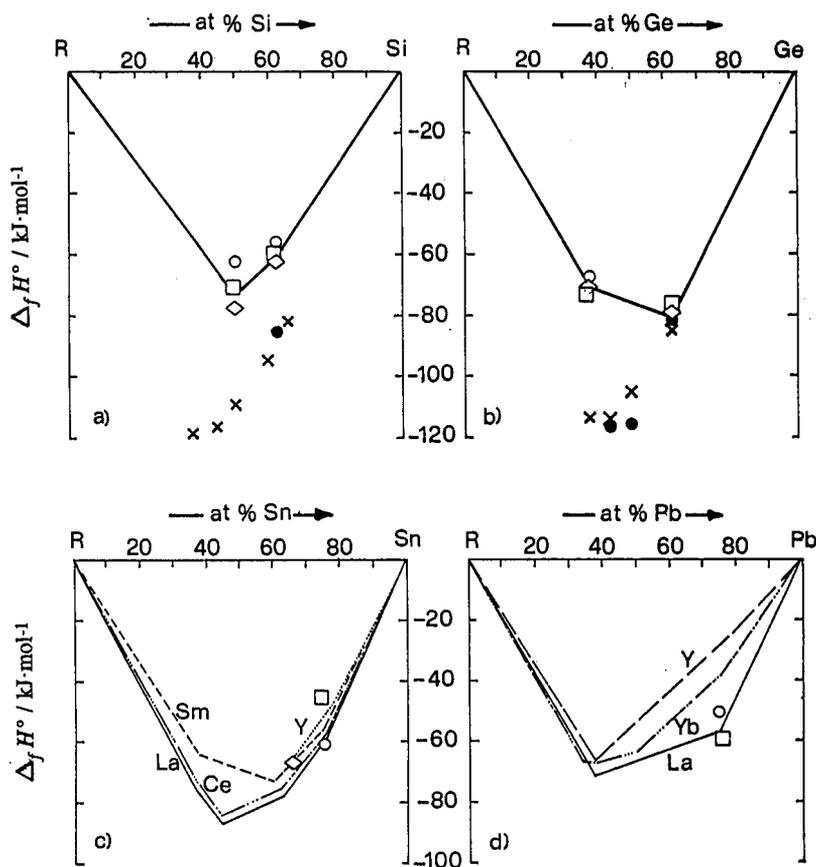


Fig. 3 Enthalpies of formation of solid R-X alloys at 300 K. Experimental data.

a) R-Si alloys: calorimetric data (34, 37): \circ La, \square Ce, \diamond Pr
emf data (35): \bullet La, \times Gd.

The more probable $\Delta_f H^\circ$ trend for R-Si alloys (R=La to Pr) is represented by the continuous line.

b) R-Ge alloys: calorimetric data (34, 39): \circ La, \square Ce, \diamond Pr
emf data (35): \bullet La, \times Gd.

Continuous line: interpolated trend for R-Ge (R=La to Pr) alloys.

c) R-Sn alloys. Data on selected compositions: calorimetric data (40-42): \circ LaSn₃, \square YbSn₃
emf data (43): \diamond YSn₂.

The trends obtained of $\Delta_f H^\circ$ vs composition are shown for La and Y (44), Ce (45) and Sm (46).

d) R-Pb alloys. Data on selected compositions: calorimetric data (47): \circ LaPb₃
emf data (48): \square LaPb₃.

The trends obtained of $\Delta_f H^\circ$ vs composition are shown for La (49), Yb (50) and Y (51, 52).

Here, too, there are large discrepancies, especially in the R-rich region, between the emf values and those obtained by calorimetry. An average trend, which is believed to be the most reliable for R = La to Pr, is also shown.

4. R-Sn Alloys High temperature emf measurements have been reported (43). Several calorimetric techniques were also used: solution calorimetry in liquid metals (40, 41), DDC (42) and direct calorimetry (45). RSn_3 alloys were studied for all the rare earths. The complete composition ranges, moreover, were investigated for Sm-Sn (46) and, in the Genoa Laboratory, for La-Sn (44) and Ce-Sn (45) systems. A few data, moreover, were reported for selected Y-Sn (44) and Lu-Sn (53) alloys. A fairly good agreement is usually found between the results for these Sn alloys from different laboratories. More work on alloys with different R could be useful in the range 40-50 at% Sn to check whether there is any change in the composition corresponding to the highest exothermic effect on passing from La to the heavier earths.

Our results are reported in Fig. 3 together with several data obtained by using different techniques.

A systematic investigation of the Nd-Sn system is in progress. The formation of NdSn_3 as the richest phase in the system and its congruent melting have been confirmed. The value of (-60 ± 2) kJ mol⁻¹ for the formation heat of NdSn_3 has now been measured by direct calorimetry. This fits well with the experimental values obtained for LaSn_3 (-60.7 ± 2) kJ mol⁻¹ and CeSn_3 (-58.6 ± 2) kJ mol⁻¹ by using the same technique.

5. R-Pb Alloys In this case too, high temperature emf techniques were employed (48, 54) as well as DDC (47) and direct calorimetry (49). Data obtained by vapour pressure measurements (55) were also reported.

In our laboratories, direct and high temperature calorimetric measurements were carried out on both solid and liquid Yb-Pb alloys (50). Sm-Pb and Gd-Pb are currently under investigation; preliminary results obtained in the measurement of formation heats at room temperature by direct calorimetry are the following: SmPb_3 $\Delta_f H^\circ = (-50 \pm 2)$ kJ mol⁻¹, GdPb_3 $\Delta_f H^\circ = (-45 \pm 2)$ kJ mol⁻¹. These values are in very good agreement with those obtained with the DDC technique (47).

For alloys with Y (51, 52) and Lu (56), emf techniques were also used. Fig. 3 summarizes typical trends of the $\Delta_f H^\circ$ of some R-Pb alloys. Since it is our main aim to obtain as complete a thermodynamic description as possible, several measurements on the phase equilibria, as well as room and high temperature diffractometric studies (57) and heat capacity measurements (58) have been carried out and are still in progress.

GENERAL REMARKS

In the light of correlations between the shape of the phase diagram and the trend in the $\Delta_f H$ as a function of composition, it might be interesting to look for a relationship between the formation heats and the melting temperature. It may be advisable to use reduced instead of absolute temperatures. For instance, in the general case of an A_{1-x}B_x compound (where A and B are the component elements), a "stability index, I_s " computed from the melting temperature has been suggested by Raynor (59, 60):

$$I_s = T_m(\text{A}_{1-x}\text{B}_x) / [(1-x) T_m(\text{A}) + x T_m(\text{B})]$$

where T_m is the melting or transformation temperature expressed in Kelvin.

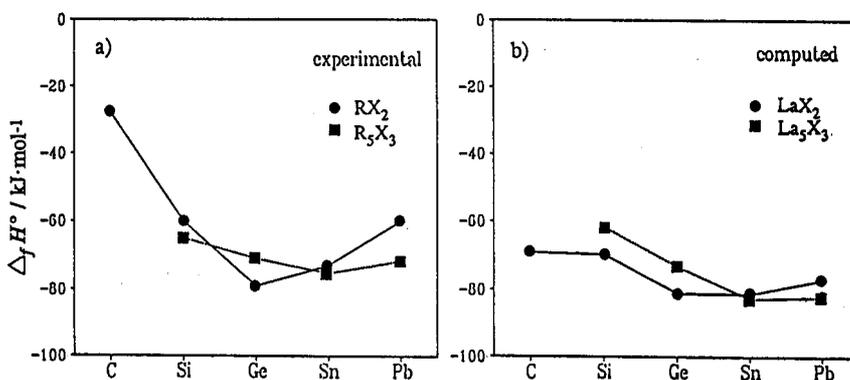


Fig. 4 Trends of the enthalpies of formation for representative compositions of solid R compounds with 14th group elements: a) the experimental data have been averaged for the light R alloys (R=La to Pr); b) the computed data are relevant to the La alloys (62).

A satisfactory comparison between I_s and the $\Delta_f H$ values has been observed in several systems (61). In our case particularly high I_s values were found for Sn and Pb alloys. These compare well with the trends of the experimental $\Delta_f H$ values reported in Fig. 4a for characteristic R_mX_n stoichiometries of R-X alloys. Comparison of the experimental values with those calculated according to the Miedema formula (62), seems to be more significant. A good agreement may be observed (see Fig. 4b) even when considering the different compositions. Discrepancies, however, occur in the case of the carbides. Here the Miedema formula does not seem to be sufficiently accurate (see for instance ref. 62 p. 56), and gives rise to clearly more exothermic values.

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