Comparison of enthalpies of formation and enthalpies of mixing in transition metal based alloys

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Abstract

Recent calorimetric investigations of enthalpies of mixing in liquid alloys and of enthalpies of formation of intermetallic compounds have brought important information in systems which present very strong heteroatomic interactions. In the light of these new data, it is possible to discuss the Miedema's formulation of enthalpies of formation and of mixing, the short range order in the liquid alloys and to propose a simple modeling of the enthalpy of mixing in transition metal–sp metal alloys. © 1998 Elsevier Science B.V.

Keywords: Calorimetry; Enthalpy of mixing; Enthalpy of formation; Enthalpy of melting; Short range order

1. Introduction

During the last twenty years numerous calorimetric investigations of metallic systems have realized a great amount of information on the enthalpies of formation of compounds and on the enthalpies of mixing in liquid alloys [1,2]. These results have been achieved owing to the development of calorimeters working at an increasingly high temperature with very acceptable precision [3–15]. Then reliable results have been obtained in systems which apparently are very difficult to study, because one or two of the constituent elements present a very high melting point or are very reactive with respect to the materials usually used.

This great amount of information especially in transition metal based alloys is very interesting for many purposes. The development of phase diagram calculations in multi-component systems needs the knowledge of the thermodynamic properties at least in the limiting binaries. Information on enthalpies of formation and enthalpies of mixing are always welcome in the optimization procedures. More the ability of empirical or purely ab initio methods to predict the thermodynamic behavior in metallic systems must be tested on experimental data. Among the thermodynamic quantities which can be derived from theoretical models in intermetallic compounds, the enthalpy of formation plays the first role. Indeed the enthalpy of formation is deduced from the cohesive energy of the considered compound and of the pure constituent elements. Using a tight binding model, Watson and Bennett [16] and Colinet et al. [17] have proposed predictions of the enthalpies of formation of disordered binary alloys of transition metals. Now more sophisticated methods applicable to a large variety of alloys are used [18,19]. These methods are based on

the calculation of the energies of formation at $T=0$ K of selected perfectly ordered compounds. The Hamiltonian of solid solutions based on various lattices may be derived using the Connolly and Williams [20] inversion scheme. The properties at non zero temperature are obtained using the cluster variation method [21,22] to treat the ordering effects and by introducing vibrational, relaxation and elastic contributions if necessary.

The field of molten alloys has been less studied, presumably because the structure of the liquid alloys is more complicated than those of intermetallic compounds. In simple metal liquid alloys, Hafner et al. [23] have proposed a simple model based on hard-spheres interacting by Coulomb or screened Coulomb (Yukawa) potentials to explain for the structure and thermodynamics when the alloys present strong chemical interactions. Very interesting results were obtained in Li–(Pb, Ag, Mg) alloys for instance [24]. From the point of view of ab initio calculations, Hafner et al. [25,26] presented calculations in liquid and amorphous alloys of simple metals. Their investigations were based on pseudopotential calculations of the atomic forces and molecular dynamic computer experiments. In transition metal based alloys, Pasturel and Hafner [27] developed a technique based on a tight-binding d-electron Hamiltonian and a thermodynamic variational method based on the Gibbs–Bogolyubov inequality and a hard-sphere Yukawa fluid as reference system.

Considering predictions of enthalpies of mixing, Miedema's empirical scheme [28–33] gives information in all possible binary alloys. However, especially in transition metal based alloys, the available data were very scarce when Miedema and coworkers [28–33] developed their empirical model. In the light of the new available experimental data it is certainly useful to give some observations and to draw some conclusions.

In numerous liquid alloys, particularly in transition metal–sp metal alloys, the presence of strong short range order has often been quoted. The most popular interpretation of the thermodynamic data in systems which display a strong non-ideal mixing behavior consists in assuming the existence of chemical complexes or associates. Extensive work using such assumption has been done for the modeling of the enthalpy of mixing in all kind of alloys: simple metal alloys, transition metal alloys, d metal–sp metal alloys, and in semi metal alloys [34–47]. However direct evidence for the existence and the form of the associates is still lacking. In this paper we will show that the modeling of the enthalpy of mixing in systems which display strong interactions is possible by using a modified version of a pair quasi chemical model.
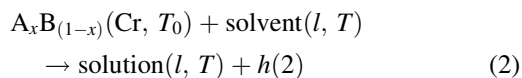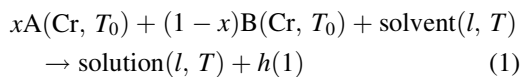
Another interesting point, which will be discussed in the light of new experimental information, concerns the difference between the enthalpy of formation of an intermetallic compound and the enthalpy of mixing of the corresponding liquid phase or, in other words, how the melting enthalpy of an intermetallic compound differs from the sum weighted by the molar fractions of the melting enthalpies of the pure constituents.

2. Calorimetric determinations of enthalpies of formation of intermetallic compounds

Different methods can be used to derive enthalpies of formation of intermetallic compounds. In the so called indirect methods, the compound (or the solid solution) is prepared and characterized before the calorimetric experiment. The drop solution calorimetry and the solute+solvent drop calorimetry belong to these indirect methods. In the direct methods, usually called direct reaction, combination or synthesis calorimetry, the reaction of formation of the compound occurs during the calorimetric experiment.

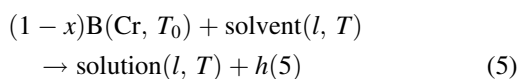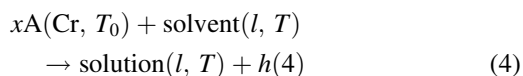### 2.1. High temperature solution calorimetry

This method was first used to obtain the enthalpy of formation of intermetallic compounds [48]. The thermodynamic basis of solution calorimetry is:

$$x\text{A}(\text{Cr}, T_0) + (1 - x)\text{B}(\text{Cr}, T_0) + \text{solvent}(l, T)$$
$$\rightarrow \text{solution}(l, T) + h(1) \tag{1}$$

$$\text{A}_x\text{B}_{(1-x)}(\text{Cr}, T_0) + \text{solvent}(l, T)$$
$$\rightarrow \text{solution}(l, T) + h(2) \tag{2}$$

The molar enthalpy of formation of the $\text{A}_x\text{B}_{(1-x)}$ compound at T_0 is obtained from the difference between the two enthalpies of solution obtained in Eqs. (1) and (2):

$$\Delta_{\text{form}}H[\text{A}_x\text{B}_{(1-x)}, \text{Cr}, T_0] = h(1) - h(2) \tag{3}$$

If the dissolutions are performed at very high dilution of the solutes A and B in the solvent the measurement of the heat of solution of the mechanical mixture xA+$(1-x)$B may be replaced by two individual measurements: the dissolutions of pure A and pure B in the solvent according to:

$$xA(Cr, T_0) + solvent(l, T)$$
$$\rightarrow solution(l, T) + h(4) \qquad (4)$$

$$(1-x)B(Cr, T_0) + solvent(l, T)$$
$$\rightarrow solution(l, T) + h(5) \qquad (5)$$

Then the molar enthalpy of formation of the $A_xB_{(1-x)}$ compound at T_0 is obtained by:

$$\Delta_{form}H_m[A_xB_{(1-x)}, Cr, T_0]$$
$$= xh(4) + (1-x)h(5) - h(2) \qquad (6)$$

Several metallic solvents have been used such as tin, aluminum, copper and germanium [48]. In practice the solution calorimetry needs a large amount of solvent to obtain a dilute solution. This requirement was often realized in low temperature calorimeters but is more difficult to realize in the twin Calvet microcalorimeter, because the diameter of the silica tube is small, or in the Setaram high temperature calorimeter. In this case other methods have been preferred and new technics developed.

2.2. Solute+solvent drop calorimetry

In this method initiated by Topor and Kleppa in 1984 [49], the compound and an adequate amount of a solvent are dropped into the calorimetric cell to generate a liquid mixture with a thermal effect of h_c, in a second experiment a mechanical mixture of the constituent elements and the solvent are introduced in the same way in the calorimeter with a thermal effect h_e. The molar enthalpy of formation of the compound is obtained by the difference $h_e - h_c$ referred to one mole of the compound. Depending on the solutes, various solvents have been used, for example pure platinum to dissolve LaB$_6$ [49] and PtSi [50], an eutectic amount of palladium (or platinum) and silicon to derive the enthalpies of formation of silicides [51] or a Pt(Pd, Ni)–Ge alloy to obtain the enthalpies of formation of germanides [52] and of transition metal alloys [53].

2.3. Direct reaction calorimetry at low temperature

When enthalpies of formation are obtained by direct reaction calorimetry, the compound is synthesized in the calorimeter and characterized after the calorimetric experiment. Depending on the calorimeter used and of the system studied, different techniques are employed.

Since 1974, Ferro and coworkers [54] have used an aneroid isoperibolic calorimeter to measure the enthalpies of formation of intermetallic compounds of rare earths and low melting elements. Because the compound cools down to room temperature in the calorimeter the enthalpy of formation is measured at room temperature. The method works for congruent melting compounds and compounds which decomposes peritectically. A great amount of information concerning rare earth and aluminum, tin, lead, bismuth and antimony alloys have been obtained by this group [55]. Recently, calorimetric investigations have been performed in the Yb–Al and La–Al systems [56].

2.4. Direct reaction calorimetry at high temperature

Using a very high temperature heat-flow calorimeter, Gachon and Hertz [14] studied several binary transition metal alloys. Small pellets of powdered components at room temperature T_0 are introduced in the calorimeter at a temperature T just below the melting point of the compound, the compound formation occurs as:

$$xA(Cr, T_0) + (1-x)B(Cr, T_0)$$
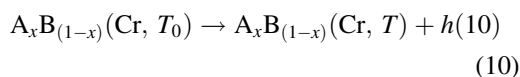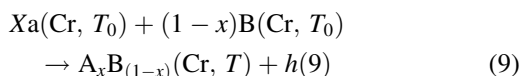$$\rightarrow A_xB_{(1-x)}(Cr, T) + h(7) \qquad (7)$$
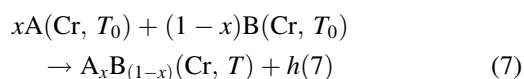
The measured heat effect $h(7)$ includes the heat content of the two pure constituents between T_0 and T and the enthalpy of formation of the compound at T. The heat contents of the pure elements between T_0 and T are found in various compilations of thermochemical data concerning the pure elements. The molar enthalpy of formation of the compound at T is obtained using the relation:

$$\Delta_{form}H_m[A_xB_{(1-x)}, Cr, T]$$
$$= h(7) - x[H_m(A, Cr, T) - H_m(A, Cr, T_0)]$$
$$- (1-x)[H_m(B, Cr, T) - H_m(B, Cr, T_0)] \qquad (8)$$

As the constituent elements are usually solid at the temperature T of the calorimeter, the enthalpy of formation is referred to the pure solid elements. A review of the results obtained by Gachon and coworkers may be found in [57,58]. More recently, calorimetric determinations have been performed in the Ru–Ge [59] and Os–Zr [60] systems.

2.5. Reaction and drop calorimetry

The same method was used by Selhaoui and Kleppa [61,62] to obtain enthalpies of formation of compounds of group VIIIA transition element with rare earth elements. In the procedure adopted by these authors, an additional measurement is made to get the enthalpy of formation at room temperature: the heat content of the compound is measured by drop calorimetry. The two calorimetric reactions are:

$$X\text{a}(\text{Cr}, T_0) + (1 - x)\text{B}(\text{Cr}, T_0) \\ \rightarrow \text{A}_x\text{B}_{(1-x)}(\text{Cr}, T) + h(9) \tag{9}$$

$$\text{A}_x\text{B}_{(1-x)}(\text{Cr}, T_0) \rightarrow \text{A}_x\text{B}_{(1-x)}(\text{Cr}, T) + h(10) \tag{10}$$

If possible the compound obtained during the Eq. (9) is used in Eq. (10). The molar enthalpy of formation of the compound is obtained by:

$$\Delta_{\text{form}}H_{\text{m}}[\text{A}_x\text{B}_{(1-x)}, \text{Cr}, T_0] = h(9) - h(10) \tag{11}$$

As the mechanical mixture of the pure elements and the compounds are dropped in the calorimeter from room temperature, the enthalpy of formation is obtained at room temperature.

Using reaction and drop calorimetry, a great number of experimental results have been obtained by Jung and Kleppa [63] and Meschel and Kleppa [64] in alloys of rare earths or transition elements with sp metals such as B, Al, C, Si, Ge, Sn and in alloys of two transition metals by Guo and Kleppa [65–68]. Often limited to compounds which melt congruently, the method has been shown to work with compounds which decompose peritectically too [69].

2.6. Mixing and drop calorimetry

For compounds which melt congruently at a temperature lower than the temperature of the calorimeter, Kleppa and Watanabe [70] proposed the following scheme. In a first calorimetric experiment, a liquid alloy is formed in the calorimetric cell according to the following reaction:

$$x\text{A}(\text{Cr}, T_0) + (1 - x)\text{B}(\text{Cr}, T_0) \\ \rightarrow \text{A}_x\text{B}_{(1-x)}(l, T) + h(12) \tag{12}$$
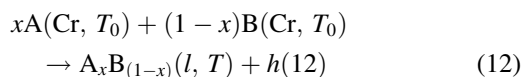
When this alloy is cooled to room temperature, the corresponding solid alloy is obtained. The heat content of the compound between the room temperature and the calorimeter temperature is measured in a second calorimetric experiment:

$$\text{A}_x\text{B}_{(1-x)}(\text{Cr}, T_0) \rightarrow \text{A}_x\text{B}_{(1-x)}(l, T) + h(13) \tag{13}$$
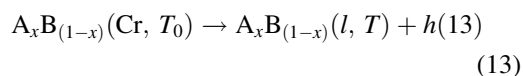
The molar enthalpy of formation of the solid alloy at room temperature is obtained by:

$$\Delta_{\text{form}}H_{\text{m}}[\text{A}_x\text{B}_{(1-x)}, \text{Cr}, T_0] = h(12) - h(13) \tag{14}$$

No additional data such as heat contents are needed to obtain the enthalpy of formation of the compound at room temperature. As we will see in the following section, the result of Eq. (12) will lead to an additional information: the enthalpy of mixing of the liquid alloy at T and for the composition x of A in the alloy, provided that the heat contents and the heat of fusion of the constituent elements are known. Systematic experimental studies using mixing and drop calorimetry have been performed by Fitzner and Kleppa [71] in alloys of noble metals with early transition metals or rare earth metals.

In the Pt–Ge system, Lbibb and Castanet [72] used either reaction and drop calorimetry or mixing and drop calorimetry depending of the temperature of the calorimeter and of the liquidus temperature. Among all the compounds displayed in the Pt–Ge system, only one is congruent melting. When the liquid alloy was cooled to room temperature, an annealing treatment for 24 h at about 150 K below the peritectic temperature was performed to ensure the homogeneity of the solid phase.

3. Calorimetric determinations of enthalpies of mixing

3.1. Partial enthalpy of mixing

When dropping solid A from room temperature in an $A_xB_{(1-x)}$ molten mixture at temperature T the following reaction occurs:

$$\delta n A(\text{Cr}, T_0) + N[A_xB_{(1-x)}](l, T)$$
$$\rightarrow (N + \delta n)[A_{(x+\delta x)}B_{(1-x-\delta x)}](l, T) + h(15) \tag{15}$$
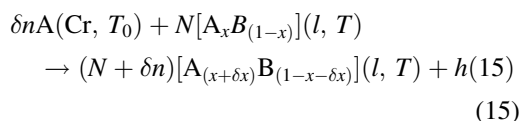
If the amount of A added to the bath is very small compared with the amount of A and B ($\delta n \ll N$), the variation of the composition is very small, $\delta x = \delta n(1-x)/(N+\delta n)$. The heat effect of Eq. (15) referred to one mole of A is the partial molar enthalpy of mixing of A in the molten alloy $A'_xB_{(1-x')}$ plus the heat content of A between T_0 and T ($x' = x + \delta x/2$). If A is liquid at T, the heat content includes the melting enthalpy. Alternatively, if A is solid at T, the partial enthalpy of A is referred to be pure A at T. If one would like to get the partial enthalpy referred to liquid A, one must subtract the molar melting enthalpy of A at a temperature which is lower than the melting temperature. This extrapolation will be discussed in Section 5.1. By measuring the partial enthalpies of mixing of the two constituents, the mixing enthalpy is obtained. This method has been used with success by Turchanin et al. [73] in rare earth–copper alloys and by Turchanin and Nikolaenko [74] in copper-transition metal alloys.

3.2. Enthalpy of mixing: mixing experiments

The enthalpy of mixing for a given composition of an alloy is obtained from the heat effect obtained in the calorimeter by dropping pure A and B with the following reaction:

$$xA(\text{Cr}, T_0) + (1-x)B(\text{Cr}, T_0)$$
$$\rightarrow A_xB_{(1-x)}(l, T) + h(16) \tag{16}$$
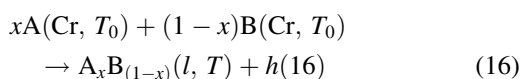
The molar enthalpy of mixing of the liquid is obtained from the heat effect of Eq. (16) and from the heat contents of pure A and B between T_0 and T:

$$\Delta_{\text{mix}}H_m^{L-L}[A_xB_{(1-x)}, l, T] = h(16)$$
$$- x[H_m(A, l, T) - H_m(A, \text{Cr}, T_0)]$$
$$- (1-x)[H_m(B, l, T) - H_m(B, \text{Cr}, T_0)] \tag{17}$$

If the pure elements are liquid at T, the heat contents of A and B are easily deduced from thermochemical tables. If A is solid at T, the enthalpy of liquid A must be extrapolated from the melting temperature. The problems related to this extrapolation are discussed in Section 5.1. However, the accessible thermodynamic data are the enthalpies of mixing referred to solid A and liquid B:

$$\Delta_{\text{mix}}H_m^{S-L}[A_xB_{(1-x)}, l, T] = h(16)$$
$$- x[H_m(A, \text{Cr}, T) - H_m(A, \text{Cr}, T_0)]$$
$$- (1-x)[H_m(B, l, T) - H_m(B, \text{Cr}, T_0)] \tag{18}$$

Several mixing experiments have been performed by Kleppa and coworkers [70,71] in noble metal based alloys.

3.3. Enthalpy of mixing: dilution experiments

Enthalpies of mixing are usually obtained by measuring the heat effects of successive additions of one of the two components of the system from room temperature in the liquid alloy of given composition. The reaction occurring in the calorimeter is:

$$nA(\text{Cr}, T_0) + N[A_xB_{(1-x)}](l, T)$$
$$= (N + n)[A_{x'}B_{(1-x')}](l, T) + h(19) \tag{19}$$
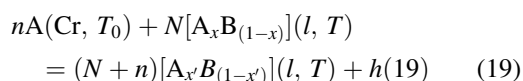
with a heat effect given by:

$$h(19) = (N + n)\Delta_{\text{mix}}H_m^{L-L}[A_{x'}B_{(1-x')}, l, T]$$
$$- N\Delta_{\text{mix}}H_m^{L-L}[A_xB_{(1-x)}, l, T]$$
$$- n[H_m(A, l, T) - H_m(A, \text{Cr}, T_0)] \tag{20}$$

When i additions of $n(i)$ mole of A to an initial amount of N_B mole of B are performed, the molar enthalpy of mixing is:

$$\Delta_{\text{mix}}H_m^{L-L}[A'_xB_{(1-x')}, l, T]$$
$$= \frac{\sum_i h(i) - \sum_i n(i)[H_m(A, l, T) - H_m(A, \text{Cr}, T)]}{N_B + \sum_i n(i)} \tag{21}$$

where $h(i)$ is the heat effect corresponding to the addition of $n(i)$ mol of A to the liquid alloy. The concentration of A in the liquid alloy after the successive additions of A is:

$$x' = \frac{\sum_i n(i)}{N_B + \sum_i n(i)} \qquad (22)$$

In dilution experiments, the values of the enthalpy of mixing depend critically on the enthalpy values which precede them in the series; the experimental errors are cumulative. However it is the method which is mostly used to get enthalpies of mixing in a large composition range.

Bros and co-workers [75–83] started the dilution experiments with a bath of the pure metal which possesses the lower melting point, then additions of the other element are performed until the solubility limit is obtained. Different sets of experiments are performed to check the validity of the values obtained at high concentration.

When measuring the enthalpies of mixing in the Pt–Si and Pd–Si systems, Topor and Kleppa [50] compared the results obtained in direct reaction and those obtained after some dilution experiments.

4. Precipitation of intermetallic compounds during calorimetric experiments

4.1. In solution experiments

When the solubility of A in B is small at the dissolution temperature, the solubility limit is reached after a few additions of the solute. Subsequent additions of A may lead to the precipitation of an intermetallic compound formed between the solute and the solvent. If we suppose the precipitated compound to have the formula $A_x B_{(1-x)}$, the precipitation reaction after the solubility limit is reached is written as:

$$x A(Cr, T_0) + N[A_{x'} B_{(1-x')}](l_{sat}, T)$$
$$\rightarrow A_x B_{(1-x)}(Cr, T) + N'[A_{x'} B_{(1-x')}](l_{sat}, T)$$
$$+ h(24) \qquad (23)$$
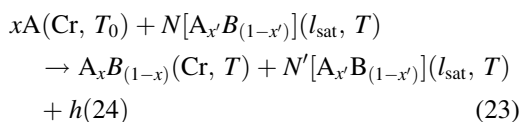
The enthalpy of formation referred to solid A and liquid B is:

$$\Delta_{form} H_m^{S-L}[A_x B_{(1-x)}, Cr, T] = h(23)$$
$$- x[H_m(A, Cr, T) - H_m(A, Cr, T_0)] \qquad (24)$$

if the solute composition at the solubility limit is small. This method has been used in systems where the solute had a low melting temperature. As this situation is not often realized this method is limited to few cases [48].

4.2. In mixing experiments

The precipitation of an intermetallic compound may also occur in dilution experiments in concentrated alloys. If the experiments are performed at a temperature which is slightly lower than the melting temperature of an intermetallic compound, the two phase domain corresponding to the equilibrium between the liquid and the intermetallic compound is reached. For the further additions, the partial enthalpies of the two constituents remain constant and the enthalpy of mixing is represented by a straight line. The results obtained in this way by Castanet [84] in the Ge–Pt system are displayed in Fig. 1 for $T=1352$ K and 1275 K. As platinum is solid and germanium liquid at the considered temperatures, the reference state of the reported values is liquid germanium and solid platinum. At 1352 K, a temperature which is higher than the melting temperature of the $Ge_{0.5}Pt_{0.5}$, the enthalpy of mixing does not reveal any special feature. At 1275 K, a temperature which is lower than the melting temperature of $Ge_{0.5}Pt_{0.5}$, a special feature is observed around the equimolar composition. Two straight lines represent the enthalpy of mixing in the two domains where the liquid phase is in equilibrium with $Ge_{0.5}Pt_{0.5}$. If the compound is perfectly stoichiometric, the two lines intersect at the exact composition of the compound. The enthalpy of formation, referred to liquid Ge and solid Pt: $\Delta_{form}H$ is the value obtained at the intersection point of the two lines (S in Fig. 1). The enthalpy of mixing for 0.5 composition is obtained by interpolation of the Δ_{mix} values between the compositions L_1 and L_2 in Fig. 1. As the enthalpy of mixing does not present any detectable variation between 1275 and 1352 K, the enthalpy of mixing at the equimolar composition can also be taken from the enthalpy of mixing curve at 1352 K.

The enthalpy of melting of $Ge_{0.5}Pt_{0.5}$ at $T=1275$ K is directly deduced from the difference between the
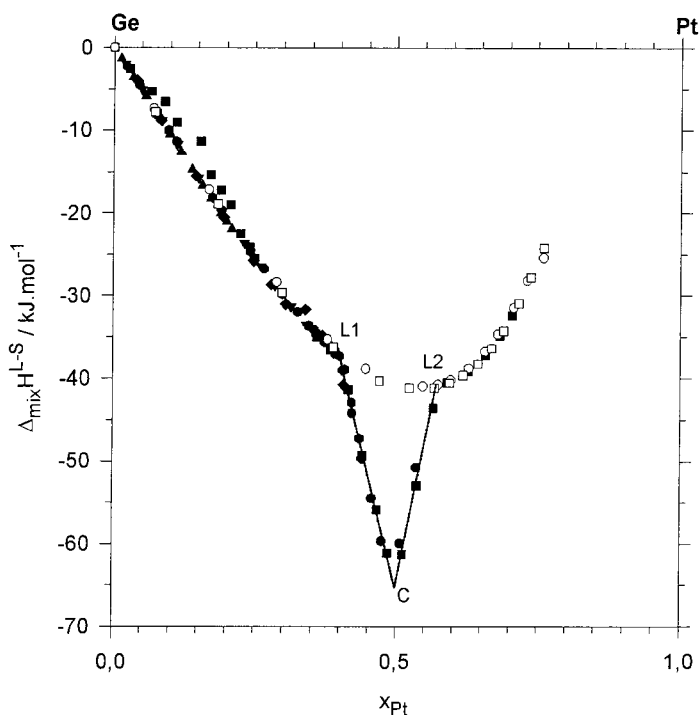
Fig. 1. Ge–Pt enthalpies of mixing referred to liquid germanium and solid platinum as obtained by Castanet [84] at 1275 K (closed symbols) and 1352 K (open symbols); the different symbols correspond to different sets of experiments.

enthalpy of mixing of the liquid at 0.5 and the enthalpy of formation of the compound provided that these two values are referred to a same reference state:

$$\Delta_{\text{fus}}H_{\text{m}}(\text{Ge}_{0.5}\text{Pt}_{0.5},\, T) = \Delta_{\text{mix}}H(\text{Ge}_{0.5}\text{Pt}_{0.5},\, l,\, T)$$
$$- \Delta_{\text{form}}H(\text{Ge}_{0.5}\text{Pt}_{0.5},\, \text{Cr},\, T) \qquad (25)$$

The method which has been explained above is very valuable because the values of the enthalpies of mixing, the enthalpy of formation of a compound and the enthalpy of melting are obtained in a same set of experiments. However, this method does not work always correctly. The viscosity of the liquid phase and the kinetics of the precipitation of the compounds are strongly temperature dependent. In the Pt–In system, where several sets of experiments have been performed at various temperatures, Anres et al. [76] observed that at temperatures lower than 1290 K, additions of platinum to a saturated liquid mixture do not lead to the formation of compounds and that $\Delta_{\text{mix}}H_{\text{m}}^{\text{L}-\text{S}}$ follows a straight line which connects the enthalpy of mixing of the saturated liquid and the zero

value of the enthalpy of mixing referred to liquid In and solid Pt. Thus the partial enthalpy of mixing of platinum referred to solid platinum is equal to zero. In the drop experiments, the measured heat effect corresponds to the heat content of platinum between room temperature and the calorimeter temperature. This phenomenon has been observed in various systems. In the case of the In–Pd system [78] at low temperature, the measured heat effect in the saturated liquid seems to correspond to the precipitation of the palladium rich solid solution because the heat effect referred to pure solid Pd is not equal to zero. In the case of the Pd–Pb system, Michel et al. [85] never obtained the precipitation of compounds though five different compounds could have precipitated in the investigated temperature range. When looking at experiences realized in alloys where one constituent has a very low melting point and the other one a very high melting point, it seems that the precipitation of one given compound is only obtained in a narrow temperature range below the melting point of this compound.

5. Discussion and conclusions

5.1. Extrapolation of the melting enthalpy of a pure element

The extrapolation of the enthalpy of melting (or of crystallization) of a pure element is needed for several thermodynamic calculations. Actually the use of thermodynamic models to describe the behavior of a system needs that the thermodynamic data of formation or of mixing are referred to the pure constituents in the same aggregation state as the considered mixture. Therefore it is often necessary to extrapolate the enthalpy of melting to temperatures which are lower than the melting point or alternatively to extrapolate the enthalpy of crystallization to temperatures which are higher than the melting point.

Experimental determinations of the enthalpies of crystallization of undercooled elements are found in the literature. Perepezko and Paik [86] determined the heat capacity of undercooled liquid metals by differential scanning calorimetry on emulsified samples, however their experimental study concerns only low melting point elements. The heat contents of undercooled Ni and Fe were measured by Barth et al. [87] using drop calorimetry combined with levitation melting. A high temperature differential calorimeter was used by Baricco et al. [88,89] to obtain the enthalpy of solidification of Ni, Fe, Cu and Pd. Wilde et al. [90] measured the heat capacity on liquid stable and undercooled pure Au and obtained undercooling levels of more than 200 K. The results presented by Barth et al. [87] and Baricco et al. [88,89] show that the heat of solidification of Ni in the undercooling domain has the same absolute value as the enthalpy of melting at the melting point. For Au Wilde et al. [90] found that the C_p curve obtained in the stable liquid domain could be extended down to an undercooling of 200 K. At this level of undercooling, they found an enthalpy of melting which is very similar to the value obtained at the melting point.

In practice, it is not uncommon to need the enthalpy of melting with a undercooling or a overheating of more than 1000 K. For example Anres et al. [77] had to calculate around 1300 K the enthalpy of crystallization of Ga to obtain the enthalpy of formation of $Ga_{0.5}Pt_{0.5}$ referred to the solid elements, and the enthalpy of melting of Pt to obtain the enthalpy of

mixing of Ga–Pt liquid alloys referred to the liquid elements. Experiments cannot be performed at such level of undercooling.

Different ways for deriving the enthalpy of melting at a temperature which is different from the melting temperature are found in the literature. The more often used method consists simply to admit that the enthalpy of melting (as well as the entropy of melting) does not depend on temperature and is the same as at the melting temperature.

In a second method, the enthalpy of fusion is obtained using the following relation:

$$
\begin{aligned}
\Delta_{\text{fus}}H_{\text{m}}(A,\,T) &= \Delta_{\text{fus}}H_{\text{m}}(A,\,T_{\text{fus}}) \\
&+ \int_{T_{\text{fus}}}^{T} [C_{p,\text{m}}(A,\,\text{l},\,T) - C_{p,\text{m}}(A,\,\text{Cr},\,T)]\,\mathrm{d}T
\end{aligned}
$$

(26)

At temperatures which are lower than the melting temperature, the enthalpy of the liquid is extrapolated to low temperatures using the heat capacity obtained in the liquid state, $C_{p,\text{m}}(A,\,\text{l},\,T)$, and the enthalpy of melting is deduced from the difference between this extrapolation and the enthalpy of the solid at the same temperature. Alternatively, at temperatures which are higher than the melting temperature, the enthalpy of the solid is extrapolated to high temperature using the analytical formulation of the heat capacity, $C_{p,\text{m}}(A,\,\text{Cr},\,T)$, below the melting temperature, then the enthalpy of melting is obtained by the difference of the enthalpy of the liquid and the extrapolation of the enthalpy of the solid to higher temperatures. Such a treatment has been used in the cases of indium and nickel. The calculated values of the enthalpy of melting as function of temperature are reported in Fig. 2(a) and (b) respectively for In and Ni. In the case of indium the procedure which has been used is misleading because solid In is predicted to be more stable than liquid In at temperatures well above the melting point. For nickel the situation is not so wrong, however an important decrease of the enthalpy of melting with decreasing temperature is observed, which seems unrealistic.

These problems are avoided if one adopts the SGTE recommendations [91]. It is suggested that at temperatures below the melting point the heat capacity of the liquid approaches that of the most stable solid
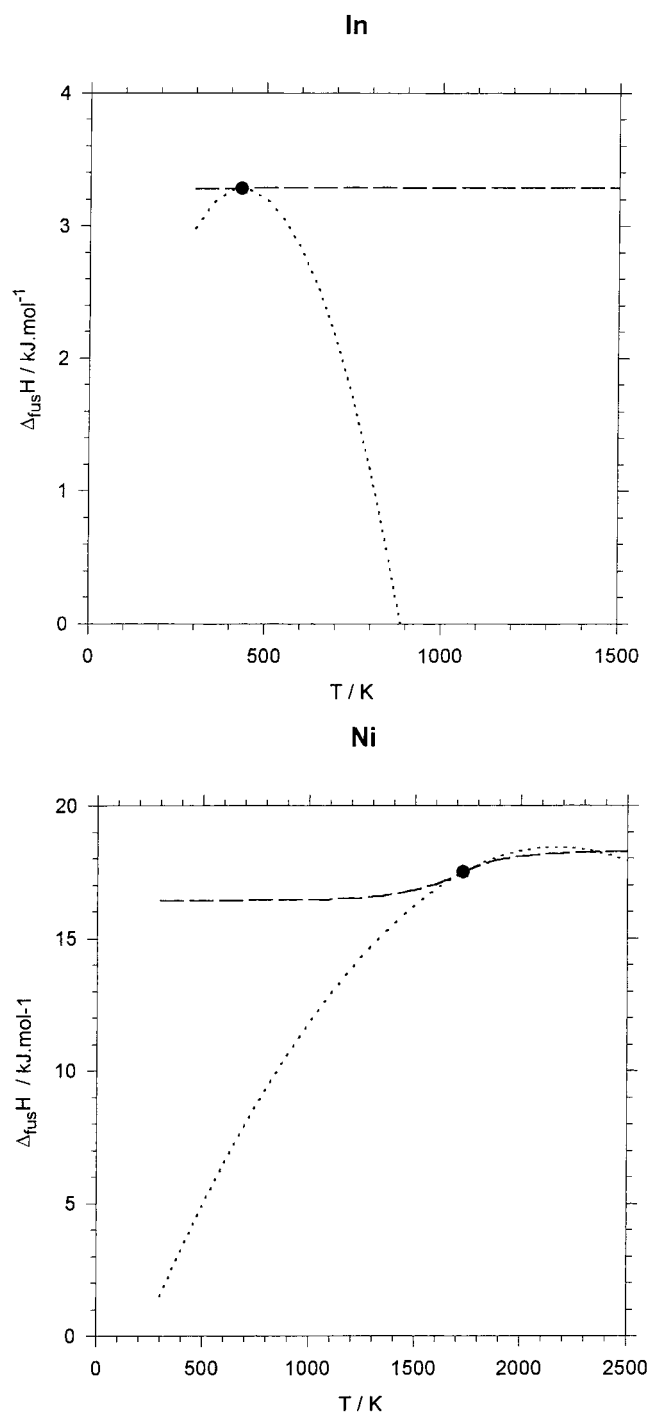
In

Ni

Fig. 2. Extrapolation of the melting enthalpy of In (a) and Ni (b). (●) experimental value at the melting point [91], (········) values obtained by extrapolation in the metastable or unstable domains of the C_p values obtained in the stable domains, (——— ——— ———) values obtained using the SGTE recommendations [91], see text for more details.

phase, and that at temperatures higher than the melting point the heat capacity of the solid phase approaches that of the liquid phase. Consequently in the SGTE pure element thermodynamic data [91], terms in T^7 and T^{-9} have been introduced in the heat capacity formulations corresponding to the liquid and to the solid respectively, in the temperature domains where these phases are metastable or unstable. In some cases a smoother extrapolation of the heat capacity of the solid and liquid phases has been proposed. The values of the enthalpies of melting of In and Ni obtained in this way are reported in Fig. 2(a) and (b) respectively; one observes that the estimated values of the enthalpy of melting are not very different from those at the melting point. However, even if the results obtained using the SGTE recommendations [91] seem to be realistic, we do not have any evidence that they are correct for temperatures very far from the melting point.

The problems drawn by the extrapolation of the enthalpy of melting of a pure element in systems where a change of reference state has to be made is rather important. Indeed several thermodynamic calculations are strongly related to this point, these are the comparisons with experimental values, the consistency of data in an optimization procedure for phase diagram calculation or discussions concerning the possible temperature variation of the enthalpy of mixing.

5.2. Melting enthalpy of intermetallic compound

The enthalpy of melting of $A_xB_{(1-x)}$ corresponds to the reaction:

$$A_xB_{(1-x)}(s, T_{fus}) \rightarrow A_xB_{(1-x)}(l, T_{fus}) \qquad (27)$$
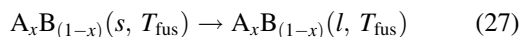
This enthalpy can be measured directly by differential scanning calorimetry. However, though such measurements are found for compounds with a low melting point [92], they are rather scarce for intermetallic compounds in transition metal based alloys because of their high melting point and their high reactivity especially in the liquid state. The enthalpy of melting may also be obtained from heat content measurements at temperatures around the melting point. For instance, Topor and Kleppa [49] used this method for the determination of the enthalpy of melting of LaB_6.

In systems where calorimetric measurements have been performed in both solid and liquid state, it is possible to calculate the enthalpy of melting of a congruent melting compound by using the relation:

$$\Delta_{fus}H_m[A_xB_{(1-x)}, T_{fus}]$$
$$= \Delta_{mix}H_m^{L-L}[A_xB_{(1-x)}, l, T_{fus}]$$
$$- \Delta_{form}H_m^{S-S}[A_xB_{(1-x)}, s, T_{fus}]$$
$$+ x\Delta_{fus}H_m(A, T_{fus})$$
$$+ (1-x)\Delta_{fus}H_m(B, T_{fus}) \qquad (28)$$

Unfortunately the use of this equation is rather limited because all the data must be obtained at the melting temperature. However, if it is assumed that the enthalpies of formation and of mixing do not vary with temperature, and that the enthalpies of melting of the pure constituents are the same as they are at their respective melting point, Eq. (28) can be written:

$$\Delta_{fus}H_m[A_xB_{(1-x)}] \approx \Delta_{mix}H_m^{L-L}[A_xB_{(1-x)}, l, T]$$
$$- \Delta_{form}H_m^{S-S}[A_xB_{(1-x)}, s, T']$$
$$+ x\Delta_{fus}H_m(A, T_{fusA})$$
$$+ (1-x)\Delta_{fus}H_m(B, T_{fusB}) \qquad (29)$$

where T and T' are the temperatures at which the enthalpy of mixing and the enthalpy of formation have been measured respectively. Besides the number of approximations made to obtain expression Eq. (29), the fact that each experimental value of the enthalpy of mixing or of the enthalpy of formation has its own uncertainty lead to use Eq. (29) with caution and to consider the result as an estimation.

Kleppa and coworkers [70,71] used the Eq. (29) to calculate the enthalpies of melting of compounds in noble metals–early transition metals or rare earth metals alloys. They obtained values which are not very different from the sum weighted by the molar fractions of the enthalpies of melting of the pure elements. The differences may be either positive or negative, the order of magnitude being less than 5 kJ/mol. Considering the uncertainties of the experimental determinations and those deriving from all approximations in the calculations, it seems difficult to derive more precise information. It is useful to remark that, with the same approximations, the enthalpy of melting can be directly evaluated from the heat effect of

reaction Eq. (13) by:

$$\Delta_{\text{fus}} H_{\text{m}}[A_x B_{(1-x)}, T_{\text{fus}}] \approx h(15)$$

$$- x \int_{T_0}^{T} C_{p,\text{m}}(A, T) \mathrm{d}T - (1-x)$$

$$\times \int_{T_0}^{T} C_{p,\text{m}}(B, T) \mathrm{d}T \qquad (30)$$

In Section 4.2 we reported on the precipitation mixing experiments where in a same set of calorimetric determinations at a given temperature the enthalpies of mixing, formation and melting are obtained, as for in transition metal–sp metal alloys [84,76–78]. Mostly the differences between the enthalpy of melting of the compound and the sum weighted by the molar fractions of the enthalpies of melting of the pure constituents is either positive or negative but small in absolute value compared to the enthalpy of melting (except in Si and Ge based alloys).

One explanation may be found when looking at Eq. (28) of the enthalpy of melting. If the difference: $\Delta_{\text{fus}} H_{\text{m}}[A_x B_{(1-x)}, T_{\text{fus}}] - [x \Delta_{\text{fus}} H_{\text{m}}(A, T_{\text{fus}}) + (1-x) \Delta_{\text{fus}} H_{\text{m}}(B, T_{\text{fus}})]$ is small in absolute value, it means that the difference: $\Delta_{\text{mix}} H_{\text{m}}^{\text{L-L}} [A_x B_{(1-x)}, \text{l}, T_{\text{fus}}] - \Delta_{\text{form}} H_{\text{m}}^{\text{S-S}} [A_x B_{(1-x)}, \text{Cr}, T_{\text{fus}}]$ is also small. In this case the enthalpy of formation is very similar to the enthalpy of mixing of the corresponding liquid phase. In systems where the chemical interactions are very strong, the major contribution to the enthalpies of formation and mixing comes from the chemical interactions. As a consequence the contribution coming from the short range order in the liquid phase is comparable to the contribution coming from the long range and short range order in the compound.

5.3. Miedema's predictions of enthalpies of mixing in transition metal based alloys

In recent years experimental investigations have been performed in liquid alloys of two transition metals or of a transition metal with a sp metal where the enthalpies of mixing are strongly negative. All these investigations give the opportunity to compare the Miedema's predictions with experimental results. Already in 1976 Boom et al. [30] observed that, in

transition metal sp metal alloys displaying strong interactions, the enthalpies of mixing were underestimated by the model; however, at that time a very restricted number of liquid alloys were already studied.

In the model proposed by Miedema [28] and improved later [29–33], the enthalpy of formation or the enthalpy of mixing results from three influences. One is the difference between the work functions, Φ^* of the pure metals, which gives a negative contribution. A second one is the discontinuity of the electron density, n_{ws}, at the boundary of the Wigner–Seitz cell, which gives a positive contribution to the enthalpy of formation. The third one, the hybridization contribution, is introduced in alloys between a d metal and a sp metal. The enthalpy of formation or the enthalpy of mixing is proportional to C defined as:

$$C = P \left[-(\Delta \Phi^*)^2 + \frac{Q}{P} (\Delta n_{\text{ws}}^{1/3})^2 - \frac{R}{P} \right] \qquad (31)$$

In this expression Δ refers to the difference of Φ^* and $n_{\text{ws}^{1/3}}$, P and Q/P are constants for large groups of alloy systems. The R term, which is introduced only in transition metal –p metal alloys, is obtained by multiplying two terms: one from the transition metal and the other one from the p metal; in liquid alloys the R value for solid alloys is multiplied by 0.73. The molar enthalpy of mixing in liquid alloy as function of composition is given by:

$$\Delta_{\text{mix}} H_{\text{m}} = x_A^s x_B^s \frac{2(x_A V_A^{2/3} + x_B V_B^{2/3})}{(n_{\text{ws}^A})^{-1/3} + (n_{\text{ws}^B})^{-1/3}} C \qquad (32)$$

In Eq. (32) a random distribution of the A and B atoms in the liquid phase is assumed. The molar enthalpy of formation of an ordered compound is given by:

$$\Delta_{\text{form}} H_{\text{m}} = x_A^s x_B^s [1 + 8(x_A^s x_B^s)^2]$$
$$\times \frac{2(x_A V_A^{2/3} + x_B V_B^{2/3})}{(n_{\text{ws}^A})^{-1/3} + (n_{\text{ws}^B})^{-1/3}} C \qquad (33)$$

The ordering effect in intermetallic compounds is taken into account in an empirical way with the term between square brackets in Eq. (33). x_i^s and V_i are the surface concentration and the molar volume of i in the alloy of composition x_i (i=A, B) respectively. The

surface concentration of A is defined as:

$$x_A^s = x_A V_A^{2/3}/(x_A V_A^{2/3} + x_B V_B^{2/3}) \qquad (34)$$

Due to charge transfer the molar volumes in the alloy are supposed to be modified with respect to the pure element volume ($V_i^{*2/3}$). The correction is given by:

$$V_A^{2/3} = V_A^{*2/3}\left[1 + a\frac{f(x)}{x_A^s}(\Phi_A^* - \Phi_B^*)\right] \qquad (35)$$

The value of the coefficient a depends on the valence of the element. This correction of the volume is often of minor importance. An iterative procedure is used to obtain the surface concentrations of A and B in the alloy.

The partial enthalpy of mixing of B at infinite dilution in A deduced from Eq. (32).

In Fig. 3 we have analyzed various f(x) functions for given values of the partial enthalpies at infinite dilution of A in B and of B in A. To simplify we have supposed these two values are equal. The curve (1) is obtained with Eq. (32); the curve (2) corresponds to a pair quasi-chemical model [93,94] where the interchange energy has been deduced from the limiting partial enthalpies of mixing; the curve (3) is obtained with Eq. (33).

When the composition dependence of the enthalpy of mixing in a liquid alloy and of the enthalpy of formation of the ordered compounds are calculated with the Miedema's model, it appears that the value of the enthalpy of mixing is always less negative than the enthalpy of formation of the ordered compounds, the difference becoming more and more important as the enthalpy of mixing becomes more negative. In transition metal–p metal alloys the difference is still more important because the value of the hybridization term R is lower in the liquid state than in solid state. In Fig. 4 the enthalpies of mixing obtained by Anres et al. [76] in In–Pt liquid alloys are displayed. The three curves have been calculated using the Miedema's model and the parameters proposed for the In–Pt system. The curve (1) is obtained using Eq. (32),
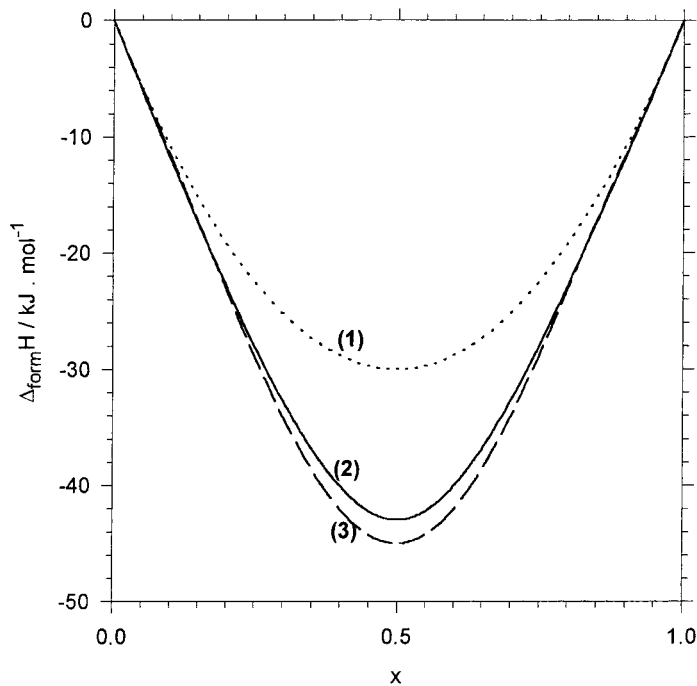

Fig. 3. Calculated values of enthalpies of mixing using the Miedema's model with a given value of C and assuming identical values of the molar volumes in the alloy. Line 1: as proposed by Miedema for liquid alloys (Eq. (34)), line 2: pair quasi–chemical model [93], line 3: as proposed by Miema for the ordered compounds (Eq. (35)).
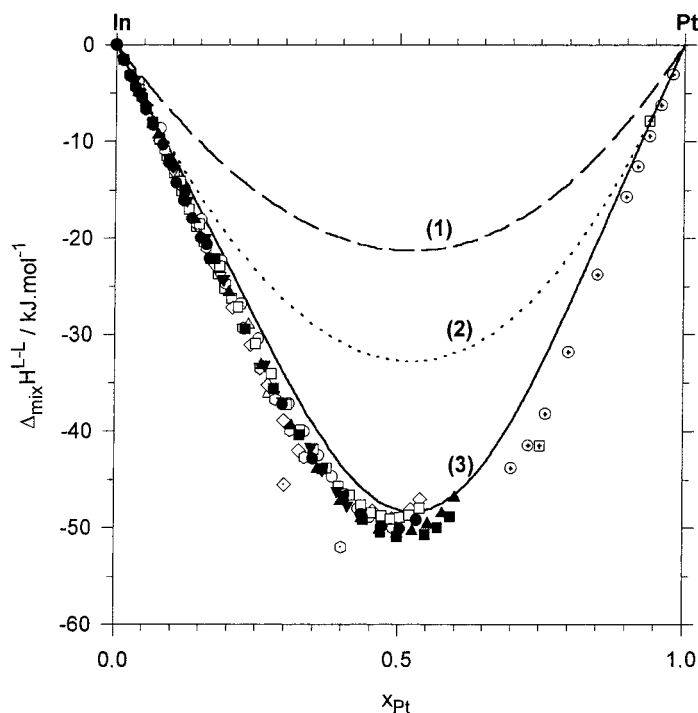
Fig. 4. Experimental values of the enthalpies of mixing (the closed and open symbols correspond to different sets of experiments [76]) and of the enthalpies of formation (⬡: [76], ◇: [98],: [96], ⊕: [98]) in the In–Pt sytem. Line 1: values reported by De Boer et al. [32] for the liquid phase, line 2: obtained with Eq. (32) but taking the *R/P* value for the solid, line 3: values reported by De Boer et al. [33] for the solid phase.

curve (2) corresponds to this calculation but with the same R/P as in the solid alloy, curve (3) is obtained using Eq. (33). If, as suggested by Anres [95], R is not reduced in the liquid compared to the solid, the values obtained for the partial enthalpies of mixing at infinite dilution are in good agreement with the experimental values. However, near equiatomic composition, the calculated values are still less negative than the experimental one, but the values predicted by Miedema et al. [33] for the enthalpies of formation of ordered compounds represent fairly well the experimental values [76] of the enthalpy of mixing [76]. The experimental values [76,96–98] of the enthalpies of formation of In–Pt compounds have been reported in Fig. 4 too. The disagreement observed between the experimental and the predicted values is in the range of uncertainty quoted by Miedema et al. [33].

Considering the set of curves drawn in Figs. 3 and 4, one may conclude that the short range order is strong in liquid In–Pt and is quite as important in the liquid phase than in the solid phase. Looking at curves

(2) and (3) in Fig. 3 one observes that a pair quasi-chemical model could be used to take into account this short range order.

5.4. Tentative modeling of the enthalpy of mixing in strong interacting systems

In the course of the present work, the question of the modeling of the enthalpy of mixing in alloys which present very strong interactions is asked. Often a Redlich Kister polynomial form is used to represent the variation with composition of $\Delta_{mix}H/x(1-x)$. This treatment of the data allows extrapolations and interpolations of the enthalpy of mixing and of the partial enthalpies, but in such treatment the presence of the short range order which appears quite as important in the liquid as in the solid state is missed. The associated model has been extensively used to explain the thermodynamic behavior of metallic systems which display strong interactions [34–47,99–102]. However, there is no physical evidence of associations in the

liquid alloys especially in transition metal alloys. In recent years Tanaka et al. [103–105] calculated thermodynamic relationships between enthalpy of mixing and excess entropy using a model based on the free volume theory.

Our purpose is to introduce the short range order by using a statistical treatment with adequate interaction terms. The cluster variation method initiated by Kikuchi in 1951 [21] and developed later by Kikuchi and numerous researchers (see [19,22] for reviews) has been used with success in solid alloys. In liquid alloys, the use of Monte Carlo or molecular dynamic simulations with appropriate interaction potentials would surly be valuable, but to our knowledge, no systematic studies have been performed in liquid alloys of transition metals. Moreover such calculations do not provide analytical expressions of the thermodynamic data which can be used directly in phase diagram calculations for instance. As it can be seen in Fig. 3, the quasi-chemical model allows to give an ordering energy which seems to have the good order of magnitude. In the following we will use a pair quasi-chemical model [93] with some modifications to be able to represent the enthalpies of mixing in a real system.

In the quasi-chemical model the energy of a phase is written as a sum of first neighbour pair interactions. When this energy is referred to the pure constituents in the same aggregation state, the molar enthalpy of mixing is given by:

$$\Delta_{\text{mix}} H_{\text{m}} = \frac{N_{Av} z}{2} \sum_{i,j} y_{ij} \Delta \varepsilon_{ij} \tag{36}$$

where N_{Av} is the Avogadro number, z the coordination number, y_{ij} the i–j pair probability and $\Delta\varepsilon_{ij}$ is related to the pair interactions ($\Delta\varepsilon_{ii}=0$, $\Delta\varepsilon_{jj}=0$). The configurational contribution to the entropy of mixing is:

$$\Delta_{\text{mix}} S_{\text{m}}^{\text{conf.}} = -N_{\text{Av}} k_{\text{B}} \left[z/2 \sum_{i,j} y_{ij} \ln y_{ij} - (z-1) \right.$$
$$\left. \times \sum_i x_i \ln x_i \right] \tag{37}$$

where x_i is the molar fraction of the constituent i. The equilibrium state is obtained by minimizing the Gibbs energy of mixing with respect to the pair probabilities. The result in a binary system is:

$$\Delta_{\text{mix}} H_{\text{m}} = x(1-x) \frac{2C}{1+D}$$

$$\text{with}: C = Nz\Delta\varepsilon_{AB}$$

$$\text{and}: D = \left[1 + 4x(1-x) \left(-1 + \exp \frac{2C}{zRT} \right) \right]^{1/2} \tag{38}$$

The enthalpy of mixing can be separated in two terms, one is the random enthalpy of mixing and is given by $x(1-x)C$ and the other one is the ordering enthalpy. The strict application of the quasi-chemical model has a double effect, the thermodynamic data of mixing are symmetrical with respect to equiatomic composition and the ordering enthalpy is related to the partial enthalpy of mixing at infinite dilution. In a real system, this does not seem realistic; indeed in the random enthalpy there are other contributions than the chemical contribution, for instance a vibrational contribution and an elastic term. It is not proved that these two terms may be written as a sum of pair interactions. In solid solutions, using the cluster Bethe lattice method or the coherent potential approximation, it is possible to calculate separately the random energy of mixing and the ordering term. Such calculations have been performed in fcc or bcc solid solutions of the Ni–Al [106] and Ni–Ti [107] systems. It is observed that the random term and the ordering term are not correlated and the random enthalpy is not symmetrical with respect to the equiatomic composition. In the case of first nearest neighbour pair interactions, the ordering enthalpy is found to be a linear function of the short range order $\sigma (\sigma = 1 - (y_{\text{AB}}/x_{\text{A}} x_{\text{B}}))$ and can be written as:

$$\Delta H^{\text{ord}} = (z/2) 4 x_{\text{A}} x_{\text{B}} V \sigma. \tag{39}$$

The effective pair interaction, V, is a function of the composition. In the modeling, we will adopt the following expression of the enthalpy of mixing:

$$\Delta_{\text{mix}} H = \Delta_{\text{mix}} H^{\text{rand}} + \Delta H^{\text{ord}}$$
$$= (1 - \xi_1^2)(A_0 + B_0\xi_1) + z/2(\xi_2 - \xi_1^2)$$
$$\times (A_1 + B_1\xi_1) \tag{40}$$

ξ_1 is the point correlation function defined as $x_{\text{A}} - x_{\text{B}}$ and ξ_2 is the pair correlation function which is related to the pair probabilities by: $\frac{1}{2}(y_{\text{AA}} + y_{\text{BB}} - 2y_{\text{AB}})$. Using Eq. (37) of the configurational entropy of mixing and
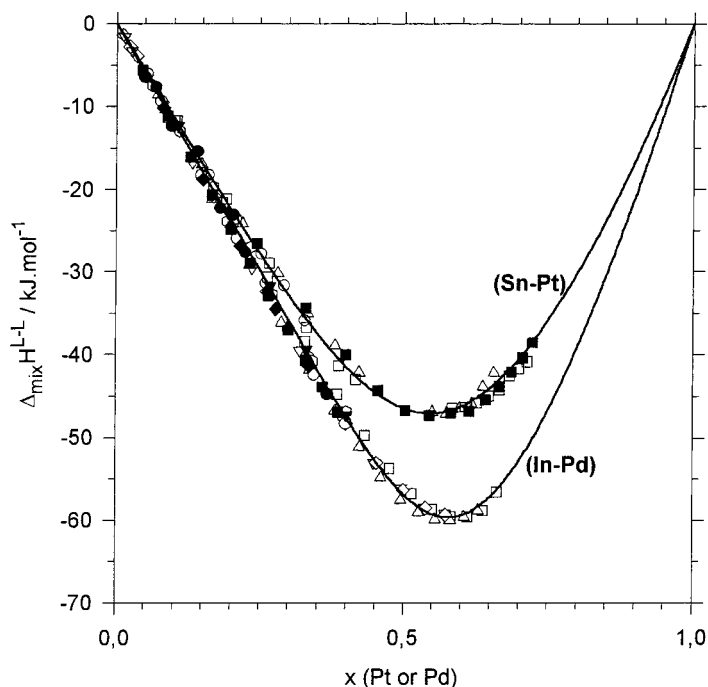
Fig. 5. Experimental values of the enthalpies of mixing in the Pt–Sn [95] and Pd–In [78] systems; the different symbols correspond to different sets of experiments. The line has been obtained using a modified pair quasi-chemical model (see text).

Eq. (40) of the enthalpy of mixing, the Gibbs energy of mixing is minimized with respect to the pair correlation function.

The modified quasi chemical model has been used in the In–Pd and Sn–Pt systems. The numerical values of A_0 and B_0 are related to the values of the partial enthalpy of A at infinite dilution in B and of B in A. The values of A_1 and B_1 are related to the values of the enthalpy of mixing with respect to the disordering term calculated with A_0 and B_0. The enthalpy of mixing as function of the molar fraction obtained in this way is displayed in Fig. 5 for the In–Pd and Sn–Pt systems. The experimental results have been obtained respectively by Hallam et al. [78] and by Anres [95]. Even if these two systems present have very similar values of the limiting partial enthalpy of mixing of Pd in liquid In and of Pt in liquid Sn, they look different. The asymmetry with respect to equiatomic composition is less pronounced in the Sn–Pt system, the enthalpies of mixing are more negative in the In–Pd system. The modeling is very satisfying in both cases.

Using this model it is also possible to give an answer to the question: why the enthalpies of mixing in the In–Pd and Sn–Pt do not vary with temperature. We have calculated the values of the enthalpy of mixing at different temperatures and observed that the short range order decreases very slowly with temperature, as a consequence the enthalpy of mixing decreases in absolute value with temperature but very slowly, this decrease it not detectable in the calorimetric experiments.

Certainly the expression of the enthalpy of mixing is more complicated than that given in Eq. (40). However, the calculation which has been performed shows that a modeling of the enthalpy of mixing is possible which introduce the short range order explicitly in the expression of the enthalpy of mixing.

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