

**SYSTEMATIC OF BINARY PHASE DIAGRAMS,
FORMED BY LOW-MELTING ELEMENTS
(Bi, Sn, Zn, In) AND THE METALS
OF IVth AND Vth PERIODS**

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Abstract

Systematic discussion of the binary phase diagrams formed by low-melting elements (Bi, Sn, Zn, In) and the metallic elements of IVth and Vth periods has been done.

Some options for theoretical prediction of the type of the phase diagrams relying on general criteria (enthalpy of formation, assessed by the Miedema model, and size factor) have been applied, and compared with experimental data about the respective binary systems. The systematization helps to determine the scope and the limits of such an approach.

These predictions have been compared with experimental data about the respective binary systems studied by the author. Forecasts for the general features of some unknown binary systems have been deduced.

Keywords: phase diagrams, dimension factor, Miedema model

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1. Introduction

The fourth and the fifth periods of the Periodic Table contain metallic elements mainly. Many of them have significant technological importance (e.g., Fe, Cu, Zn, Ni, Mn, Cr, Ti, Sn etc.). Most of their binary systems with low-melting metals (Bi, Sn, Zn, In) are studied (more or less) [1]. Anyhow, phase diagrams of some systems (Bi-Sc, Zn-Sc, Sn-Rb, Sn-Sc, In-Ru, In-Rh) have not been published, although the formation of the respective binary compounds is known. For the systems Sn-Tc, In-Tc, Bi-Tc there is no data about the presence of miscibility gaps or compounds.

The purpose of the present work is to be looked for some options for theoretical analyses of the type of the phase diagrams, relying on general semi-empirical criteria (enthalpy of formation, assessed by the Miedema model [2-5], and the size factor).

Thus, the partial molar enthalpies of formation of binary liquid solutions of metallic elements belonging to the IVth and Vth periods, at infinite dilution in solvents Bi, Sn, Zn or In have been used. The values of these quantities as assessed by Niessen et. al [4] have been used in the present analyses. For the sake of brevity, they are called “Miedema enthalpies” or “enthalpies of formation” as well.

In many cases such enthalpies of formation agree relatively well with the corresponding experimental values. A good example has been recently given by G. Borzone et al. [6].

The size factors for the various couples of atoms have been calculated using values for the empirical radii of the elements [7]. The empirical radii of Bi, In, Sn and Zn, in that order, are: $r_{\text{Bi}}=160$ pm, $r_{\text{Sn}}=145$ pm, $r_{\text{Zn}}=132$, and $r_{\text{In}}=155$. The size factor is associated with the relative difference between the atomic radii of a couple of elements and is calculated by using the ratio:

$$\left| r_A - r_{X \text{ or } Y} \right| / (r_A + r_{X \text{ or } Y}) / 2 \quad (1)$$

where r_A and $r_{X \text{ or } Y}$ are, respectively, the empirical radii of Bi, Zn, Sn or In, and of the element X (X - metal of IVth, and Y metal of the Vth period).

As supplemental criteria for the analyses are used the conventions that the formation of intermediate phases could be considered as witness for an

ordering trend, while the appearance of miscibility gap indicates the predominance of repulsion forces among the atoms of the components of a phase.

2. Discussion

2.1. Discussion of the phase diagrams Bi-X and Bi-Y

In Fig. 1 the Miedema enthalpies of formation of liquid alloys Bi-X at infinite dissolution (with bismuth solvent) are plotted as function of the atomic number of the metals X. Concerning the phase diagrams Bi-X (X – metal of the IVth period), miscibility gaps form in systems exhibiting positive enthalpies of formation (e.g., Bi-Cr, Bi-Fe, Bi-Co). This observation is in agreement with the general theoretical considerations. Nevertheless, in the respective Bi-Y phase diagram (Y – metal of the Vth period) miscibility gaps are not observed (Fig. 1), although there are systems (e.g., Bi-Mo, Bi-Ru) whose deviations from the ideal behaviour are as strong as these in the systems Bi-Cr and Bi-Fe (Fig. 1).

In Bi-X and Bi-Y systems, exhibiting feeble Miedema enthalpies of formation of liquid alloys, neither miscibility gaps, neither intermediate compounds form (e.g., Bi-Cu, Bi-Ge, Bi-Cd, Bi-Ag, Bi-Sn, Bi-Sb).

Phase diagrams, with intermediate compounds, are regularly associated with Bi-X and Bi-Y systems, characterised by negative Miedema enthalpies of formation of liquid (e.g., Bi-K, Bi-Ca, Bi-Sc, Bi-Ti, Bi-Rb, Bi-Sr, Bi-Y, Bi-Zr, Bi-Pd). The thermodynamic behaviour of this kind of systems is the most consistent among all the considered combinations (Fig. 1).

Systematic of the Bi-X and Bi-Y phase diagrams interrelated with the size factor and the partial molar enthalpies of mixing at infinite dissolution [4] of the respective liquid alloys is shown in Fig. 2. One can see that Bi-X and Bi-Y systems possessing intermediate compounds are characterized by negative enthalpies of mixing and do not depend on the size factor.

Liquid phase miscibility gaps are formed, as expected, in systems with positive mixing enthalpies and size factor values disposed in the interval 0.13 to 0.21. Diagrams without miscibility gap in the liquid phase, and without

intermediate compounds can form in systems with positive Miedema enthalpies of mixing and at arbitrary values size factor. Thus, it is not possible to predict with high precision (on the basis of the Miedema enthalpies of mixing only) whether a miscibility gap will appear in a system with positive deviations from the ideal thermodynamic behavior.

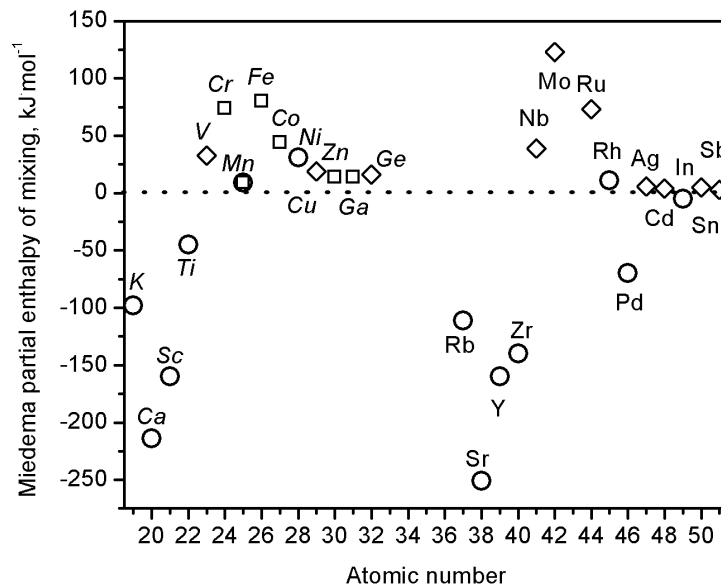


Fig. 1. Interrelation between the atomic number (plotted along the abscissa) and the respective partial molar enthalpies of mixing at infinite dissolution [4] of binary Bi-X and Bi-Y liquid alloys (with bismuth as solvent); X - metal of the IV-th period, Y - metal of the V-th period; O - phase diagram with intermediated compounds; □ - diagram with miscibility gap in the liquid phase; ◇ - diagram without miscibility gap in the liquid phase and without intermediated compounds. Standard states are the liquid phases of the respective components.

2.2. Discussion of the phase diagrams Zn-X and Zn-Y

In Fig. 3 one can see that intermediate compounds form in each system Zn-X or Zn-Y exhibiting negative partial molar enthalpy of mixing at infinite dissolution [4] of liquid alloys. This is also valid for systems with very feeble negative enthalpies of mixing (e.g. Zn-V, Zn-Nb and Zn-Sb).

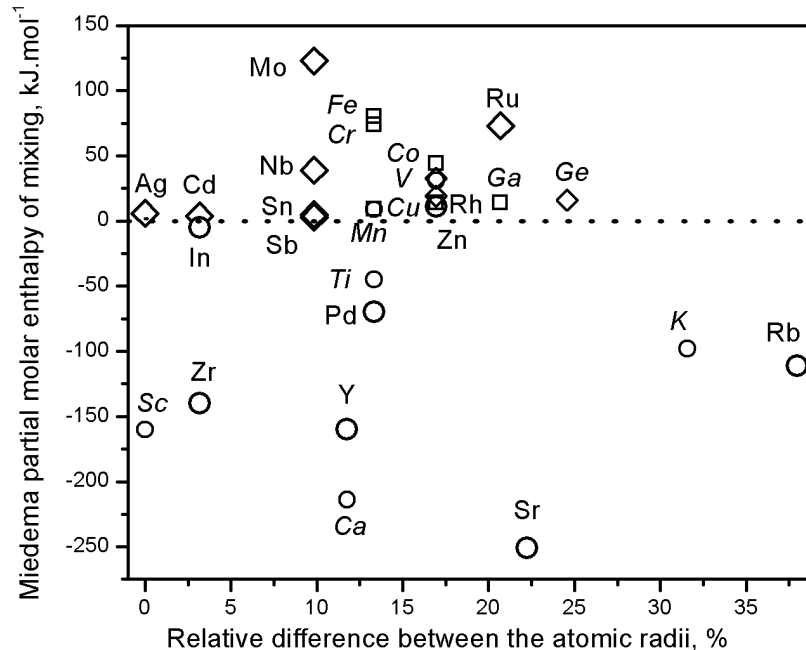


Fig. 2. Systematic of the Bi-X and Bi-Y phase diagrams (X - metal of the IV-th period, Y - metal of the V-th period). The relative difference between the atomic radii (i.e. size factor) is plotted along the abscissa, and the respective partial molar enthalpies of mixing at infinite dissolution [4] of binary Bi-X and Bi-Y liquid alloys (with bismuth as solvent) is shown along the ordinate axis. O - phase diagram with intermediated compounds; □ - diagram with miscibility gap in the liquid phase; ◇ - diagram without miscibility gap in the liquid phase and without intermediated compounds. Standard states are the liquid phases of the respective components.

Miscibility gaps in the liquid phase are observed in the systems Zn-alkaline metal (Zn-K, Zn-Rb) only. Obvious reason is the rather unfavourable size factor (difference of more 50 %) (Fig. 4).

Another conclusion is that intermediate phases do not appear in systems with feeble positive mixing enthalpies of the liquid phase. The system Zn-Mo having medium strong positive mixing enthalpies of the liquid phase is an exception.

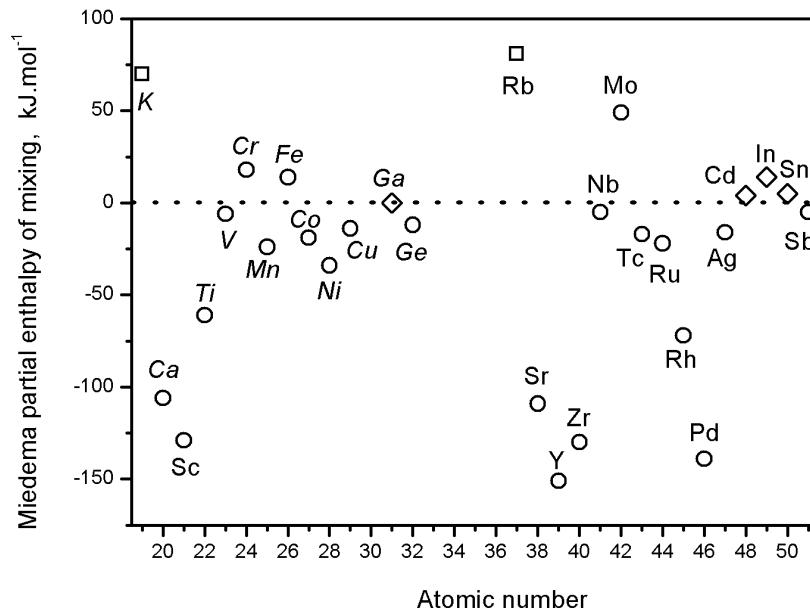


Fig. 3. Interrelation between the atomic number (plotted along the abscissa) and the respective partial molar enthalpies of mixing at infinite dissolution [4] of binary Zn-X and Zn-Y liquid alloys (with zinc as solvent); X - metal of the IV-th period, Y - metal of the V-th period; O - phase diagram with intermediated compounds; □ - diagram with miscibility gap in the liquid phase; ◇ - diagram without miscibility gap in the liquid phase and without intermediated compounds. Standard states are the liquid phases of the respective components.

2.3. Discussion of the phase diagrams Sn-X and Sn-Y

Similarly to the previously discussed cases (Bi- and Zn-phase diagrams) all systems Sn-X and Sn-Y (Fig. 5) exhibiting negative molar enthalpies of mixing at infinite dissolution consistently form intermediate compounds. The system Sn-Mo shows untypical behavior (similarly to the system Zn-Mo) having large positive enthalpy of formation but forming intermediate phases. It is interesting to notice that the empirical atomic radii of both elements are equal (0.145 pm [7]).

Miscibility gaps in liquid phase are observed in the systems Sn-Cr, Sn-Fe and Sn-V. The size factors of these systems are favorable (equal to or less than 7 %, Fig. 6), consequently, the appearance of the miscibility gaps is due to thermodynamic factors.

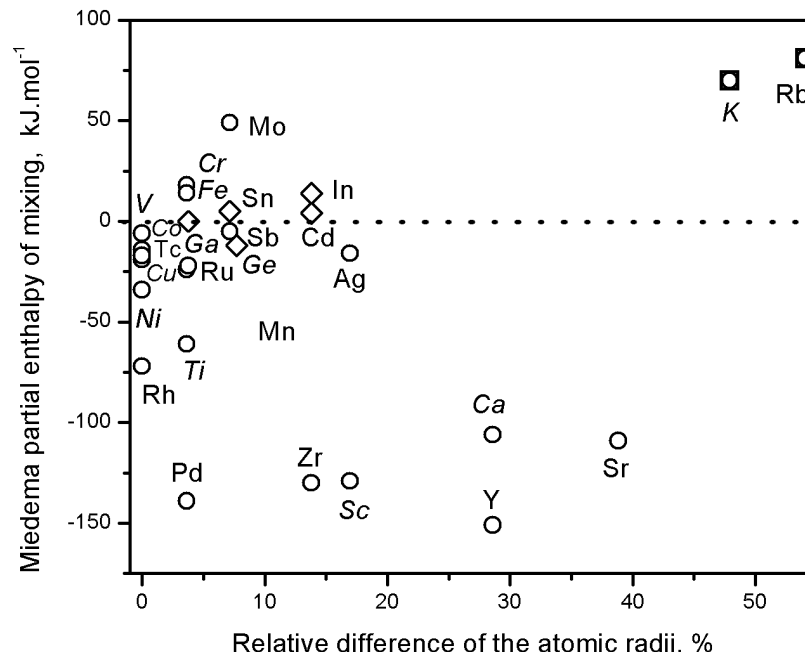


Fig. 4. Systematic of the Zn-X and Zn-Y phase diagrams (X - metal of the IV-th period, Y - metal of the V-th period). The relative difference between the atomic radii (i.e. size factor) is plotted along the abscissa, and the respective partial molar enthalpies of mixing at infinite dissolution [1983Nie] of binary Zn-X and Zn-Y liquid alloys (with zinc as solvent) is shown along the ordinate axis. O - phase diagram with intermediated compounds; □ - diagram with miscibility gap in the liquid phase; ◇ - diagram without miscibility gap in the liquid phase and without intermediated compounds. Standard states are the liquid phases of the respective components.

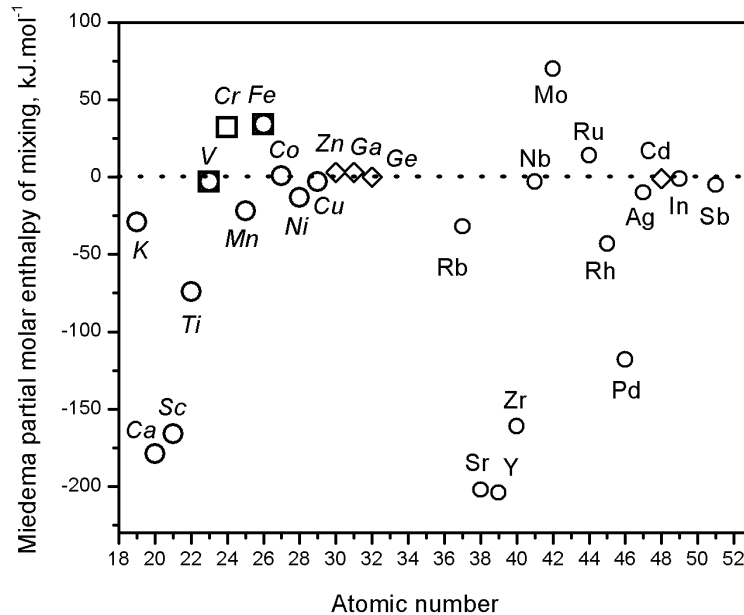


Fig. 5. Interrelation between the atomic number (plotted along the abscissa) and the respective partial molar enthalpies of mixing at infinite dissolution [4] of binary Sn-X and Sn-Y liquid alloys (with tin as solvent); X - metal of the IV-th period, Y - metal of the V-th period; O - phase diagram with intermediated compounds; □ - diagram with miscibility gap in the liquid phase; ◇ - diagram without miscibility gap in the liquid phase and without intermediated compounds. Standard states are the liquid phases of the respective components.

2.4. Discussion of the phase diagrams In-X and In-Y

Miscibility gaps appear in several In-X and In-Y systems (In-K, In-V, In-Fe, In-Co, In-Rb (Fig. 7)). Their formation in the systems In-K and In-Rb (both possessing negative Miedema enthalpies of mixing) is probably due to the unfavourable size factor (difference of more than 35 %, Fig. 8).

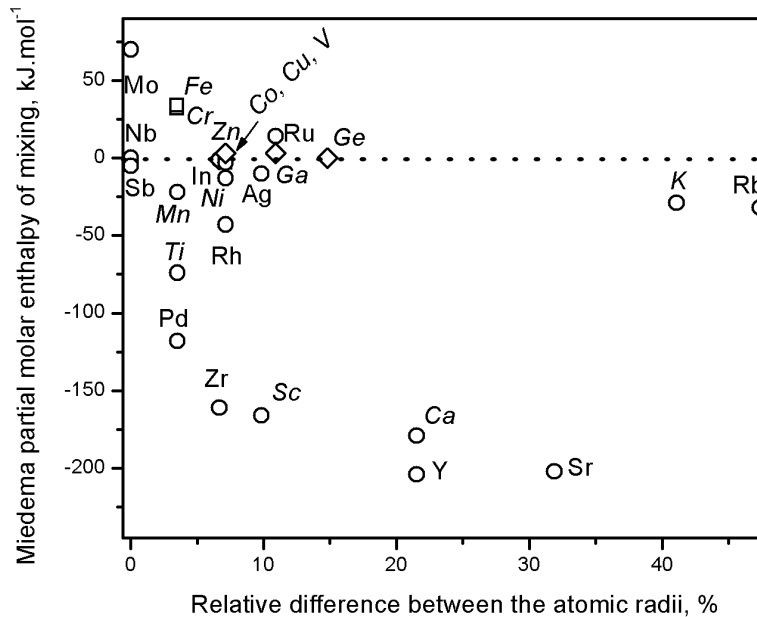


Fig. 6. Systematic of the Sn-X and Sn-Y phase diagrams (X - metal of the IV-th period, Y - metal of the V-th period). The relative difference between the atomic radii (i.e. size factor) is plotted along the abscissa, and the respective partial molar enthalpies of mixing at infinite dissolution [4] of binary Sn-X and Sn-Y liquid alloys (with tin as solvent) is shown along the ordinate axis. O - phase diagram with intermediated compounds; □ - diagram with miscibility gap in the liquid phase; ◇ - diagram without miscibility gap in the liquid phase and without intermediated compounds. Standard states are the liquid phases of the respective components.

3. General Discussion and Conclusion

Two criteria (enthalpy of formation, assessed by the Miedema model and size factor) have been applied in order to analyze systematically the phase diagrams M-X and M-Y (M is Bi, Zn, Sn or In). The multitudes of these systems have been regarded as belonging to some of the following phase diagram types: A) phase diagram with formation of miscibility gaps in liquid phase, and B) phase diagram with formation of intermediate compounds.

The phase diagrams lacking both - intermediate compounds and miscibility gaps in liquid phase are regarded as a third type (C), closely related with the previous two.

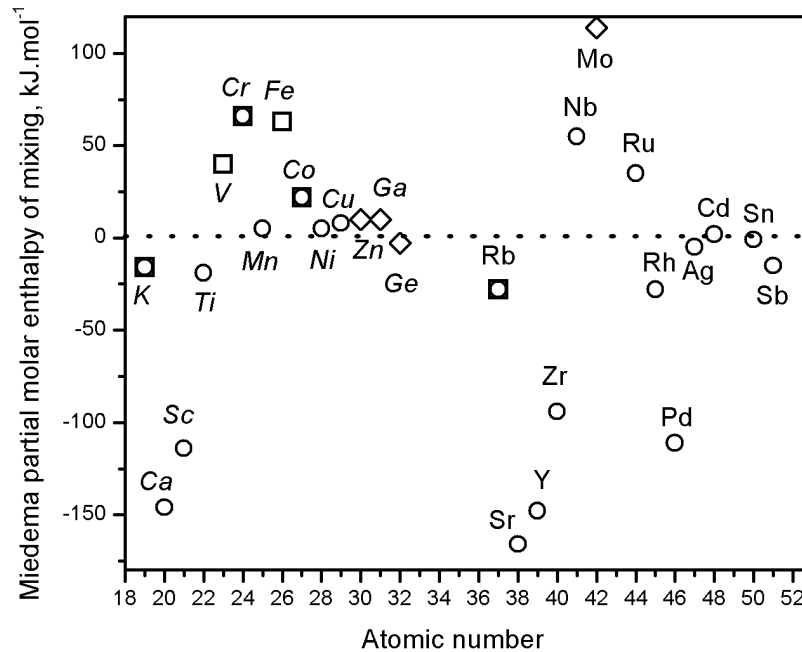


Fig. 7. Interrelation between the atomic number (plotted along the abscissa) and the respective partial molar enthalpies of mixing at infinite dissolution [4] of binary In-X and In-Y liquid alloys (with indium as solvent); X - metal of the IV-th period, Y - metal of the V-th period; O - phase diagram with intermediated compounds; □ - diagram with miscibility gap in the liquid phase; ◇ - diagram without miscibility gap in the liquid phase and without intermediated compounds. Standard states are the liquid phases of the respective components.

A. Phase diagrams with miscibility gaps in liquid phase

As a rule (with some exceptions) miscibility gaps form in systems exhibiting significant positive enthalpies of mixing (assessed by means of the

Miedema method). As a general exception, we should notice that the bismuth does not form liquid phase miscibility gaps with the metallic elements of the fifth period.

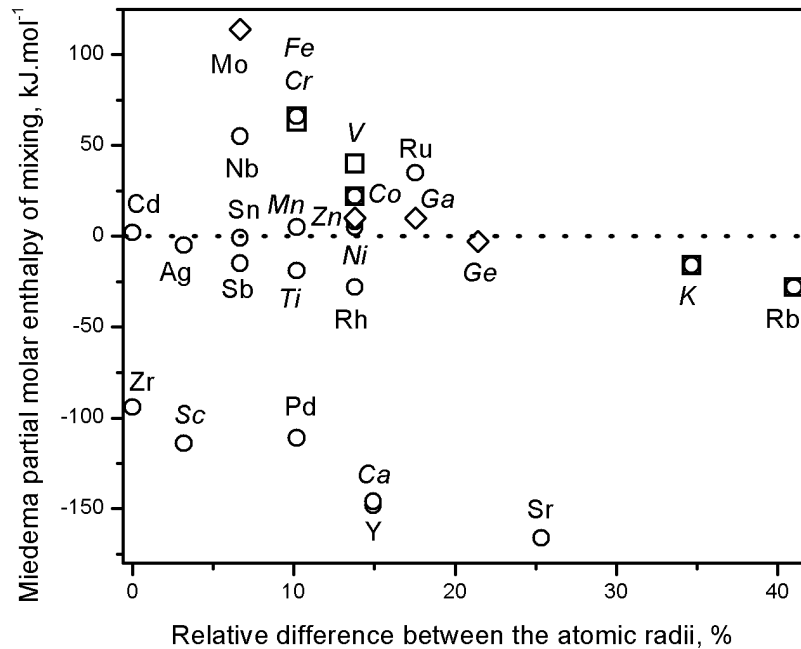


Fig. 8. Systematic of the In-X and In-Y phase diagrams (X - metal of the IV-th period, Y - metal of the V-th period). The relative difference between the atomic radii (i.e. size factor) is plotted along the abscissa, and the respective partial molar enthalpies of mixing at infinite dissolution [4] of binary Sn-X and Sn-Y liquid alloys (with indium as solvent) is shown along the ordinate axis. O - phase diagram with intermediated compounds; □ - diagram with miscibility gap in the liquid phase; ◇ - diagram without miscibility gap in the liquid phase and without intermediated compounds. Standard states are the liquid phases of the respective components.

B. Diagrams with formation of intermediate compounds

Generally, intermediate compounds are observed in systems having negative Miedema enthalpies of mixing.

Bismuth forms intermediate compounds with alkaline and alkaline-earth metals of the fourth and fifth periods (K, Ca, Rb, Sr), as well as with the first two neighbors transition elements (Sc, Ti and Y, Zr). In this array are classified the systems Bi-Mn, Bi-Ni, Bi-Rh, Bi-Pd and Bi-In, too.

Zinc does not form intermediate phases with K and Rb, but forms such with Cr, Fe, Mo (although they all have positive mixing enthalpies). One is aware that the most important factor for the formation of these phases is the electron concentration, but this factor is out of the scope of the present analyzez. Similar exceptions are registered among the systems Sn-Y (Sn-Mo, Sn-Ru) and In-Y (In-Nb).

C. Phase diagrams without intermediate compounds and without miscibility gaps in liquid phase

Such diagrams are, usually, typical for systems exhibiting feeble positive Miedema mixing enthalpies in liquid phase: Bi-Ge, Bi-Ag, Bi-In, Bi-Sn, Bi-Sb, Zn-Ga, Zn-In, Zn-Sn, In-Ga as well as others. Influence of the size factor on the phase formation in such kind of systems has not been found out.

The above-developed systematic of the binary systems, formed by low-melting elements (Bi, Sn, Zn, In) and the metals of IVth and Vth periods presents a broad-spectrum frame where one can arrange the phase diagrams (Sn-Co, Zn-Co, Zn-Ni, Zn-Ti, Bi-Ti, Bi-Ni) studied by the author [8-17].

Some characteristics (Miedema enthalpies and size factors) of these systems are represented in Table 1. Comparing the experimental data the results of pertinent thermodynamic optimisations the influence of the values for Miedema enthalpies and size factors, one can deduce that the considered systems behave in agreement with the above-done general conclusions. Actually, all these systems exhibit medium negative (Zn-Co, Zn-Ni, Zn-Ti, Bi-Ti) or positive (Sn-Co, Bi-Ni) Miedema enthalpies of formation of the liquid phase. Thus, intermediate compounds are observed in each of the diagrams. In the systems where the size factors are the most favorable (Zn-Co and Zn-Ni) some of the intermediate phases subsist in significant homogeneity ranges (e.g., β and γ -phases).

It is interesting to notice that that the sign of the Miedema enthalpies of formation of the liquid phase are, probably, related with the solid-state solubility of both constituents. For example, one observes significant solubility of Zn and Bi in the solid Co, Ni and Ti (systems with negative Miedema enthalpies). Contrary, in the systems with positive Miedema enthalpies (Sn-Co, Bi-Ni) the solubility of Sn and Bi is rather limited [1]. This topic might merit further attention but, actually, it is out of the scope of the present discussion.

Table 1. Characteristics of the binary phase diagrams, studied by the author: Miedema enthalpy (kJ/mol) - partial molar enthalpies of mixing at infinite dissolution of the metallic elements (Ti, Ni, Co) in Bi, Sn, Zn and In solvents, according to Niessen et al. [4]; Size Factor (%) - relative difference between the empirical atomic radii of the respective pairs.

System	Miedema enthalpy, kJ/mol	Size Factor %
Bi-Ni	+31	17
Bi-Ti	-45	13
Sn-Co	1	7
Zn-Ni	-34	0
Zn-Co	-19	0
Zn-Ti	-61	4

As mentioned in the beginning there are some Tc and Bi-, Sn- and In-based systems lacking experimental information for them. The Miedema enthalpies and the size factors calculated for these systems are shown in Table 2. The expected types of the corresponding phase diagrams are shown there as well. Surely, future experimental studies are needed in order to find out the exact features of the discussed systems.

In a few above-shown cases the peculiarity of Mo binary systems has been underlined (they exhibit large positive Miedema enthalpies of mixing but do not form miscibility gaps). Nevertheless, this is partially true, only.

Table 2. Characteristics of some Sn-Tc and In-Tc phase diagrams, missing experimental data. Miedema enthalpy (kJ/mol) - partial molar enthalpies of mixing at infinite dissolution of the metallic elements (Ti, Ni, Co) in Sn and In solvents, according to Niessen et al. [4]; Size Factor (%) - relative difference between the empirical atomic radii of the respective pairs. Expected phase diagram type, according to the present systematic: m.g. - miscibility gap; w.c. - phase diagram without intermediate compounds; i.c. - phase diagram with intermediate compounds.

System	Miedema enthalpy, kJ/mol	Size Factor %	Expected phase diagram type
Bi-Tc	+75	17	m.g. or w.c.
In-Tc	+39	14	m.g. or w.c.
Sn-Tc	+16	7	i.c. or w.c.

The physical reason for the described behavior becomes clear if one takes into account the huge difference of the melting and boiling temperatures of Mo, from one side, and Bi, In, Zn and Sn, from the other side. For example, the molybdenum melting point is 2623 °C, while the boiling points of Bi, In, Zn and Sn are 1564, 2073, 907 and 2603 °C (thus, the liquid phase, rich in the low-melting elements, is not stable at the molybdenum melting point). Thus, the liquid phases rich in the low-melting elements are not stable at temperatures equal or higher than the molybdenum melting point. That is why, the lack of a liquid phase miscibility zone in such a system might be formal only. Such considerations are to be taken into account when analyses of similar systems have to be done.

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