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Abstract

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PHYSICAL CHEMISTRY

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ON THE ASYMMETRY OF MUTUAL SOLUBILITY IN METALLIC SYSTEMS

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It has been established that, when many metals interact with other elements, continuous and limited solid solutions and intermetallic compounds are formed (1-3). The principal condition determining the type of interaction of metals is the similarity or difference in the electronic structure, sizes, electronegativity values, and ionization potentials of the atoms of the elements. With complete similarity, or with only a small difference in these metallochemical properties of the elements, continuous solid solutions are formed; with some degree of difference, only limited solid solutions are formed. In the latter case, many experimental data show that the limiting concentrations of the mutual solubility of the components in one and the same A—B system are not the same. As a rule, component A is only slightly soluble in component B, or, conversely, component B has high solubility in component A. Cases of approximately equal solubility of the components in each other in one and the same system are quite rare.

Fig. 1. Two types of equilibrium diagrams: **A**—with asymmetric mutual solubility, **B**—with symmetric mutual solubility.

Thus, in metallic systems there is a clear inequality of the mutual limiting solubility of the components. If, on the equilibrium diagram of a binary system, a conventional vertical axis of symmetry is drawn through 50 at.% of the components, then with respect to this axis of symmetry, in the overwhelming majority of systems, we shall have an asymmetry of the mutual solubility of the components.

Without considering the question of the interaction of metals in binary systems as a whole, we present here (Fig. 1) two equilibrium diagrams (schematic) of binary systems with limited solubility and the formation of one compound. Let us suppose that the composition of this compound corresponds to the equiatomic ratio 1 : 1. In this particular case its composition will constitute the axis of symmetry.

In one diagram (Fig. 1, A) a considerable solubility of component B in component A and a very small solubility of component A in B are shown, while in the second diagram (Fig. 1, B) approximately equal limiting solubility of both components is shown. Consequently, it may be considered that in the first system asymmetry exists, while in the second case there is symmetry of the limiting solubility of the components.

Before giving an answer to the question of the cause of such asymmetry and symmetry of the mutual solubility of components in metallic systems, let us present some factual data.

An analysis of information on phase diagrams of binary metallic systems—from silver to zirconium according to Hansen (4)—shows that cases of asymmetric mutual limiting solubility predominate. This is especially clearly revealed in analyzing data on mutual solubility in systems composed of transition-group metals and aluminum, tin, beryllium, and other more electronegative elements than the transition-group metals. This proposition is also valid in metal–metalloid systems, where the electronegative elements (B, Si, C, P, etc.) are more soluble in electropositive metals than vice versa.

Let us consider some data on the mutual solubility of components in systems composed of transition-group metals with aluminum and tin. Table 1, after (4, 5), gives such data. In all cases, the solubility at the solidus point on the melting diagram is taken as the limiting solubility.

Table 1

Mutual solubility of transition-group metals, aluminum, and tin

Group of the periodic system	Aluminum systems	Solubility at the solidus point, at. %* A in B	Solubility at the solidus point, at. %* B in A	Tin systems	Solubility at the solidus point, at. %* A in B	Solubility at the solidus point, at. %* B in A
IV	Ti–Al	<0.1	48.5	Ti–Sn	<0.1	16.0
IV	Zr–Al	<0.1	26.0	Zr–Sn	<0.1	~17.0?
IV	Hf–Al	–	–	Hf–Sn	?	?
IV	Th–Al	<0.1	~3.0	Th–Sn	?	?
V	V–Al	<0.1	49.5	V–Sn	<0.1	~10.0
V	Nb–Al	~0.1	10.0	Nb–Sn	?	?
V	Ta–Al	~0.1	~	Ta–Sn	?	?
VI	Cr–Al	~0.7	45	Cr–Sn	insol.	~40?
VI	Mo–Al	<0.1	19.5	Mo–Sn	?	?
VI	W–Al	<0.1	14.5	W–Sn	?	?
VI	U–Al	<0.1	6.0	U–Sn	?	?

Group of the periodic system	Aluminum systems	Solubility at the solidus point, at. %* A in B	Solubility at the solidus point, at. %* B in A	Tin systems	Solubility at the solidus point, at. %* A in B	Solubility at the solidus point, at. %* B in A
VII	Mn—Al	<0.1	42.0	—	0.1	8.7
VII	Re—Al	—	—	—		
VIII	Fe—Al	<0.1	52.0?	Mn—Sn	<0.1	8.3
VIII	Ru—Al	—	—	Re—Sn	?	?
VIII	Os—Al	—	—	Os—Sn	—	?
VIII	Co—Al	<0.1	15.0	Co—Sn	<0.1	2.5?
VIII	Rh—Al	—	—	Rh—Sn	<0.1	~10?
VIII	Ir—Al	—	—	Ir—Sn	<0.1	
VIII	Ni—Al	<0.1	21.0	Ni—Sn	<0.1	10.4
VIII	Pd—Al	<0.1	18.0?	Pd—Sn	<0.1	~9.5
VIII	Pt—Al	<0.1		Pt—Sn	<0.1	~8.0

* In the listed systems: A—the transition metals, which are electropositive; B—aluminum, which is electronegative.

The data presented in Table 1, unfortunately, are not yet complete. There is especially little information on systems with tin. Nevertheless, as is evident from these data, the transition-group metals (A) are negligibly soluble in aluminum or tin (B). Their solubility in many systems does not exceed 0.1%. However, the solubility of both of these metals (B) in the transition-group metals (A) is high. Moreover, a clear sequence is observed in the decrease of solubility by groups, as the atomic number increases.

Such a sequence in the decrease of the limiting solubility of aluminum or tin in metals of groups IV—V—VI is clearly revealed in se···

curves shown in Fig. 2. Although complete literature data are available only for the metals of group V (Cr—Mo—W—U), it may be assumed that a successive decrease in the solubility of aluminum should also exist for the remaining groups.

Using this proposition, by methods of extrapolation or interpolation along these curves one can determine the possible limiting solubility of certain metals in these groups. Thus, for example, by extrapolating the solubility curve of Al in Ti and Zr to the metals Hf and Th, one can assert that the limiting solubility of Al in these metals will be less than in Ti and Zr, and that it will decrease successively from Ti to Th, as is shown by the dashed line on the curve (Fig. 2).

The same sequence in the change of solubility in metals of the transition groups can be shown by the example of other electronegative elements, for example tin

Fig. 2. Limiting solubility of Al in metals of the transition (IV—VI) groups

Figure 2: Fig. 2. Limiting solubility of Al in metals of the transition (IV—VI) groups

(see Table 1), beryllium, silicon, etc. Without entering into a detailed analysis of the data for approximately equal mutual solubility of the components, it may be said that this occurs in systems where the metallochemical properties favor the formation of limited solid solutions, but in electronegativity they differ little from one another. To these systems, to some extent, may be assigned Ag—Cu, Cr—Ni, W—Hf, Mo—Hf, and some others.

On the basis of an analysis of the predominance of asymmetry of mutual limiting solubility in metallic systems, one may arrive at the establishment of the following principal regularities:

1) In the interaction of metals of the transition groups with more electronegative metals, their limiting solubility in the latter is negligible, whereas the solubility of electronegative metals in them is high.

Fig. 2. Limiting solubility of Al in metals of the transition (IV—VI) groups

2) Maximum solubility is observed in metals of group IV with the maximum number of unfilled electrons in the *d*-shell.
3) Within one and the same group, the limiting solubility decreases as the electropositivity of the metal increases (from Ti → Zr → Hf → Th), i.e., as the difference in electronegativity of the interacting metals increases.
4) The indicated solubility also decreases as the atomic number increases by periods and as the electrons in the *d*-shell of the atoms are gradually filled; it corresponds to the series: Ti → V → Cr → Mn → Fe → Co → Ni.

From the regularities listed above for the asymmetry of mutual limiting solubility in systems of metals of transition groups with certain electronegative elements, the following general conclusion may be drawn: the limiting solubility of an electronegative element will be greater in an electropositive metal and, conversely, the least solubility in the same system will be that of the electropositive metal in the electronegative element. Consideration of all binary systems according to Hansen (4) from this point of view in the overwhelming majority of cases confirms the rule stated above by us. Some exception occurs for the metals of group VIII.

In the present work, without analyzing in detail the reasons for the existence of the asymmetry of mutual solubility that we have established, we shall note only the following: such an asymmetry in the mutual solubility of components is apparently determined by the asymmetry of the electronic structure of the interacting atoms in the given system.

Electropositive metals—other conditions being equal—have more "free" outer electrons in the atomic lattice; when other elements dissolve in them, they are capable of accepting a larger number of electrons from atoms of electronegative elements into the common pool of conduction electrons without the formation between them of directed chemical bonds characteristic of compound formation. The negligible solubility of electropositive metals in electronegative ones is explained by the greater tendency of the latter to accept electrons and thereby form directed bonds between electrons of unlike atoms. As a consequence, at negligible solubility based on electronegative elements, metallides are formed predominantly in the systems. Moreover, as a rule, the compositions of these compounds are characterized by the maximum number of atoms of the electronegative elements.

Thus, for example, at nearly negligible solubility in aluminum, in the systems Ti–Al, V–Al, Cr–Al, Mn–Al, Fe–Al, aluminides rich in aluminum are formed: $TiAl_{12}$, VAl_{11}, $CrAl_7$, $MnAl_6$, $FeAl_3$; the same is also the case in the formation of beryllides, etc.

But these questions, connected with the compositions of metallides and the ratio of atoms of electropositive and electronegative elements in compounds, deserve separate consideration.

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