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Abstract

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A METALLOCHEMICAL TABLE OF THE CHEMICAL ELEMENTS

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Recent studies have shown the very important role of D. I. Mendeleev' s periodic law of the chemical elements in the development of the chemistry of metallic alloys (^1), or, as we now call it, metallochemistry (^2), which deals with the study of the chemical interaction of metallic elements with one another or with metalloids in cases where the latter form solutions and compounds with a metallic type of bond.

From a general point of view, the interaction of metals is characterized by the formation of two classes of complex substances—metallic solutions and metallic compounds. A distinctive feature of metals is their great tendency to form solid solutions over broad ranges of concentration. Metallic compounds, as a rule, do not obey the theory of valence and in most cases possess metallic properties. Compounds with metallic properties are also formed as a result of the interaction of metals with certain metalloids, such as, for example, boron, carbon, silicon, nitrogen, and others. These compounds, no less than metals, are inclined to form solid solutions with one another or with metals.

The special features of the chemical interaction of metals with the elements of the periodic system provide grounds for distinguishing a special table of the chemical elements, which makes it possible to give a classification of solid solutions and compounds of metals and to trace the gradual transition from metallic compounds to compounds of metals of the ionic type. We call such a table the metallochemical table of the chemical elements, by analogy with the geochemical table of the elements proposed by A. E. Fersman (^3) and other authors (^4).

In the geochemical table of the elements, groups of elements occurring jointly or separately under natural conditions are distinguished; i.e., the natural position of the elements in nature is recorded. The metallochemical table of the elements makes it possible to unite elements of the Mendeleev system that are similar and different in their properties into families for the synthesis of various types of metallic formations, beginning with solid solutions and metallic compounds and ending with compounds of constant composition with an ionic character of bonding.

Figure 1 presents such a metallochemical table of the chemical elements, showing families of metals capable of forming: 1) continuous solid solutions, 2) limited solid solutions with metallic compounds, 3) metallic compounds without solid solutions, 4) compounds of ionic type, and 5) a group of elements incapable of interacting with the metals of the family located in the middle part of the periodic system.

It is evident from the table that the character of the interaction is determined by the mutual position of the metallic elements in the periodic system and, conse-

respectively, by their electronic structure, as well as by atomic and ionic radii. The latter, as is known, vary regularly from element to element by groups and periods.

On the basis of an analysis of the families of metals distinguished in the metallochemical table, it may be said that the formation of solid solutions is most characteristic of metals located in the middle part of the expanded Mendeleev table, and especially of elements of the transition groups with an unfilled (d)-electron shell. They have similar chemical properties

[Figure 1: Metallochemical table of the chemical elements.]

*–lanthanides
**–actinides

a –metals forming continuous solid solutions;
b –metals forming limited solid solutions, metallic compounds;
c –metalloids forming limited solid solutions;
d –metalloids forming ionic compounds;
e –metals incapable of interaction with metals of the middle part of the periodic system of elements

Fig. 1. Metallochemical table of the chemical elements: (a) –metals forming continuous solid solutions; (b) –metals forming limited solid solutions, metallic compounds; (c) –metalloids forming limited solid solutions; (d) –metalloids forming ionic compounds; (e) –metals incapable of interaction with metals of the middle part of the periodic system of elements

and only a small difference in atomic radii. For example, the family of metals forming continuous solid solutions is made up of metals of the same groups of the periodic system. This is shown in the interaction of metals of such groups as group IV ((Ti–Zr–Hf)), group V ((V–Nb–Ta)), and group VI ((Cr–Mo–W)), and of a number of metals of groups VII and VIII, with the exception of metals with a non-isomorphous crystal structure, for example Mn and Re, Fe and Ru, etc.

The tendency toward the formation of continuous solid solutions within groups, given similarity of electronic structure, closeness of atomic radii, and isomorphism of structure, is also manifested in cases of interaction between analogous elements possessing metallic or even metalloid properties. Thus, for example, in the group of alkali metals, continuous solid solutions are formed between analogues: potassium and cesium, cesium and rubidium; the same continuous solid solutions are formed in the systems: germanium—silicon, arsenic—antimony, and antimony—bismuth.

The tendency toward the formation of solid solutions in the family of these metals decreases by periods in passing from analogous metals to metals that differ in their properties, or successively in passing from one group to another. This corresponds to the change in their chemical properties. Thus, the tendency toward the formation of solid solutions for metals of group VIII decreases from right to left, and for metals of group IV—from left to right.

For example, for Ni this decrease in solubility is expressed by the following series:

$$\mathrm{Ni} \rightarrow \mathrm{Co} \rightarrow \mathrm{Fe} \rightarrow \mathrm{Mn} \rightarrow \mathrm{Cr} \rightarrow \mathrm{V} \rightarrow \mathrm{Ti} \rightarrow \mathrm{Sc} \rightarrow \mathrm{Ca} \rightarrow \mathrm{K}.$$

In the series of these elements up to manganese, nickel forms continuous solid solutions; from chromium to Ti only limited ones; and with Ca and K it does not interact at all. For titanium, a metal of group IV, the opposite picture is observed. The solubility of elements in titanium decreases according to the following series:

$$\mathrm{Ti} \rightarrow \mathrm{V} \rightarrow \mathrm{Cr} \rightarrow \mathrm{Mn} \rightarrow \mathrm{Fe} \rightarrow \mathrm{Co} \rightarrow \mathrm{Ni}.$$

Titanium with vanadium and chromium at high temperatures forms continuous solid solutions, while with Mn, Fe, Co, Ni it forms only limited ones. At the same time, the limiting concentration of the metals of limited solubility in titanium also decreases successively from Mn to Ni, i.e., as the metals become more distant from titanium ([5]).

The formation of metallic compounds with limited solubility, with a gradual transition of these into compounds with an ionic character of bonding without solid solutions, occurs for the family of those metals which are located in different groups and are considerably removed from one another ([6]). For the formation of such compounds, the interaction of metals of the main and secondary groups of subgroups A and B of the periodic system of the elements is especially characteristic (see Fig. 1).

For example, it is known that magnesium is capable of giving, with elements situated near it in the periodic system (Cu, Ag, Au, Cd, etc.), along with typical metallic compounds, solid solutions. As the elements become more distant from the magnesium group, their ability to form solid solutions with magnesium decreases, but the tendency to form compounds with a valence ratio of atoms increases: Mg_2Si, Mg_2Ge, Mg_3Bi_2, etc.

It is very characteristic that the group of elements belonging to the semimetals (Ge, As, Sb, etc.) is characterized by a slight ability to form solid solutions with typical metals, including magnesium, but these elements have a great tendency to form compounds of the semiconductor type. Such compounds include Mg_3As_2, Mg_3Sb_2, NiAs, CoAs, CoSb, InSb, etc.

Among the elements belonging to the family of metalloids, two groups should be distinguished, one of which constitutes the group of metalloids with small atomic radius (boron, carbon, nitrogen, hydrogen, and partly oxygen). This group is capable of forming with metals of the main groups limited solid solutions of the interstitial type, as well as compounds with a metallic character of bonding, with a gradual transition from metallic to ionic bonding. Such compounds as borides, carbides, and nitrides are typical metallic compounds, while oxygen compounds are either semiconducting or ionic.

The metalloids silicon and phosphorus, having atomic radii close to those of metals of the main group, also belong to the group of elements forming with these metals limited solid solutions and metallic compounds of the silicide and phosphide type.

The second group of metalloids of groups VI and VII (sulfur and haloids) belongs to the family of elements incapable of giving solid solutions with metals, but with a great tendency to form typical compounds of the ionic type. In this connection it is characteristic that the compounds of the type—first from the metal—$Me_{xR}y$, possess to some degree metallic properties (for example, NiS); compounds richer in sulfur (for example, NiS_2) have semiconducting properties, while haloid compounds of metals are typically ionic.

Among the metallic elements, the metals of the alkali and alkaline-earth groups occupy a special position in interaction with metals.

They, with the exception of lithium, beryllium, and magnesium, have maximum atomic radii, which differ markedly from the atomic radii of most other metals and metalloids. They constitute a family of metals incapable of forming solid solutions with many metals either by substitution of solvent atoms or, still less, by interstitial incorporation into the lattice of the solvent metal.

The special position of this group of metals is characterized by the fact that they are capable of interacting only with one another and with the metals of subgroup B that have high values of atomic radii, but are not capable of interacting with metals of the first family.

When the metals of this group interact with elements of the side groups of the periodic system, metallic compounds are also formed, with a gradual transition, in interaction with typical metalloids, to ionic compounds.

Thus, as a result of a brief analysis, it may be said that the metallochemical table makes it possible, in general form, to consider questions of the chemical interaction of metals with one another and with metalloids. It makes it possible, from the position of metals in the periodic system and from the chemical properties that follow from this, to determine what kinds of interaction a given metal is capable of entering into with other elements of the periodic system.

From this table one can determine the possibility of formation of solid solutions, metallic and ionic compounds for each of the metals occupying a definite place in the periodic system of the elements, and show which metals do not interact and form neither solid solutions nor compounds. The metallochemical table of the elements facilitates the classification of the various kinds of chemical interaction of metals in the formation by them of metallic alloys of different composition and structure.

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CITED LITERATURE

1. N. V. Ageev, *Chemistry of Metallic Alloys*, Publ. House of the Academy of Sciences of the USSR, 1941.

2. I. I. Kornilov, Collection of reports at the conference on the theory of metallic alloys, Publ. House of the Academy of Sciences of the USSR, 1952, p. 77.

3. A. E. Fersman, *Selected Works*, Publ. House of the Academy of Sciences of the USSR, 3, 1955, p. 61.

4. A. N. Zavaritskii, *Introduction to Petrochemistry*, Publ. House of the Academy of Sciences of the USSR, 1944, p. 10.

5. I. I. Kornilov, P. B. Budberg, *Uspekhi khimii*, **25**, No. 12, 1935 (1956).

6. I. I. Kornilov, Publ. House of the Academy of Sciences of the USSR, OKhN, 1953, 795.

Note: Figure translations are in progress. See original paper for figures.