1231 (1956).
95. B.H.Chase, G.W.Kenner, and A.R.Todd, J.Chem.Soc., 1371 (1956).
96. H.A.Staab, Chem.Ber., 89, 1927 (1956).
97. T.M.Jacob and H.G.Khorana, Chem.and Ind., 932 (1962).
98. G.Scheurbrandt, A.M.Duffield, and A.L.Nussbaum, Biochem.Biophys.Res.Comm., 11, 152 (1963).
99. Y.Lapidot and H.G.Khorana, J.Amer.Chem.Soc., 85, 1365 (1963).
100. Y.Lapidot and H.G.Khorana, J.Amer.Chem.Soc., 85, 3852 (1963).
101. H.Schaller and H.G.Khorana, J.Amer.Chem.Soc., 85, 3841 (1963).
102. G.Weimann, H.Schaller, and H.G.Khorana, J.Amer.Chem. Soc., 85, 3835 (1963).
103. P.T.Gilham and G.M.Tener, Chem.and Ind., 542 (1959).
104. E.Cherbuliez and J.Rabinowitz, Helv.Chim.Acta, 39, 1461 (1956).
105. R.W.Chambers, J.G.Moffatt, and H.G.Khorana, J.Amer. Chem.Soc., 79, 3747 (1957).
106. F.Cramer and G.Weimann, Chem.Ber., 94, 996 (1961).
107. R.Kuhn and H.J.Hass, Angew.Chem., 67, 785 (1955).
108. F.Cramer and K.H.Scheit, Angew.Chem., 74, 717 (1962).
109. G.Brewerman and E.Chargaff, J.Amer.Chem.Soc., 75, 2020 (1953).

Institute of Biological
Physics, USSR Academy
of Sciences

U.D.C. 546.3-19:543.547

# RECENT DEVELOPMENTS IN METAL CHEMISTRY

I.I.Kornilov

CONTENTS

1. Historical 31
2. Definition of the science of metal chemistry 31
3. Principal factors which determine the interaction between metals 32
Atomic radii 32
Position in the electronegativity series of the elements 32
Valency and ionisation potential 34
4. Formation of solid solutions of metals 34
5. Formation of intermetallic compounds 38
6. Crystal chemical reactions in metallic systems 42
7. Interaction between intermetallic compounds 44

## 1. HISTORICAL

Metals and alloys have played an important role in the development of human civilisation since the earliest times. However, they have only been the object of scientific investigation since the 17th–18th centuries. The development of the chemical approach to the formation of alloys is discussed in a number of papers [1-6].

Mendeleev's Periodic Law[7] of the chemical elements was by far the most important single contribution to the understanding of the regularities of chemical interactions between metals. The application of this law to the study of interactions between metals is due to Kurnakov[8]. It was he who proposed the term "metallic compounds or metallides", now widely used in the chemistry and physics of metals and in metal science, for the compounds formed by the combination of metals. The term will be used in the present article [but is hereafter translated "intermetallic compounds" (Ed. of Translation)].

The thermodynamic works of Gibbs[9] were of the utmost relevance to the development of equilibrium studies in chemical systems, including metallic systems. His papers on heterogeneous equilibria, as interpreted by Kurnakov, led to the creation of an international language based on the geometrical representation of the equilibrium diagrams of systems. Since the beginning of the 20th century, the work of Tammann[10], Roberts-Austen[11], Le Châtelier[12], and Howe[13] has contributed to progress in this direction. Systematic studies of metal interactions and of equilibrium and phase transformation diagrams received further impetus from the general advances in physicochemical analysis[14,15], metallography[16-19], and physical metallurgy[20-23].

## 2. DEFINITION OF THE SCIENCE OF METAL CHEMISTRY

The chemical approach to the science of alloys, which began with Kurnakov's application of the Periodic Law and with his equilibrium studies, has been called the chemistry of alloys[24,25], but is now unified under the general heading of metal chemistry[26-28]. This science straddles the boundary between inorganic and physical chemistry, and is also related to crystal chemistry, solid state physics, and metallography.

The general problems with which metal chemistry is concerned, identified during its development, were formulated as follows in a paper[28] presented to the Plenary Session of the Division of Chemical Sciences of the Academy of Sciences of the USSR in 1956: "the study of chemical interactions involving the metallic elements of the Periodic Table, with each other or with metalloids, with formation of solutions and compounds showing metallic and covalent bond character, and the establishment of the general principles underlying the formation, structure, and properties of this broad range of solutions and compounds of metals as a function of their composition".

Metal chemistry is a subdivision of inorganic chemistry, dealing with the formation (as a result of the interaction between atoms of metals and metalloids) of solid solutions or of intermetallic compounds of variable or fixed composition. These compounds do not, as a rule, obey the theory of valency thus: the chemistry of metallic solutions and intermetallic compounds is richer and more comprehensive than the chemistry of compounds of non-metals.

There is no class of inorganic (or, indeed, of organic) compounds, in which the tendency towards isomorphic substitution or introduction of foreign atoms into the crystal lattice is developed as strongly as in the formation of various metallic solid solutions. In this respect, only the very large number of naturally occurring inorganic materials is at all comparable with metallic solid solutions and intermetallic compounds: these are the minerals, which can show a strong tendency towards isomorphic substitution of compounds within a series (for example, oxides, sulphides, silicates, etc.), and iron meteorites, which consist mainly of solid solutions of iron, nickel, and cobalt.

Metal chemistry encompasses the chemical reactivity problems of more than 80 metals of the Periodic Table. Many products of the reaction of metals with non-metals (boron, carbon, silicon, and to a lesser extent oxygen, nitrogen, etc.) also show metallic or covalent bond character. Solutions and compounds of metals with these non-metals are also studied in metal chemistry, and in many respects these compounds can be visualised as cross-links between purely metallic compounds and compounds having a covalent or ionic bond character.

It is the purpose of metal chemistry to study: (1) the principal factors which determine the interaction between metals; (2) the formation of solid solutions between metals; (3) the formation of intermetallic compounds; (4) the crystal chemistry of reactions in metallic systems; (5) interactions between intermetallic compounds.

These problems continue to be the object of extensive investigations by chemists, physicists, and metallurgists. Very many papers in this field have been published in the past 50 years. A number of contemporary problems in metal chemistry were discussed at a special symposium on the physical chemistry of metallic solutions held in London[29].

## 3. PRINCIPAL FACTORS WHICH DETERMINE THE INTERACTION BETWEEN METALS

The conditions leading to the formation of complex substances with metallic bond character have not yet been definitely established. Problems concerning the electron distribution and the chemical bond character in complex metallic solutions and intermetallic compounds are particularly difficult. However, there are a few generally accepted physicochemical factors[18-29] which appear to determine, largely if not completely, the conditions of formation of metallic solid solutions and intermetallic compounds.

The most important condition for characterising the reactions between metals is their relative position in the Periodic Table, which determines similarities and differences in the electronic structure of the atoms and in the physicochemical properties of the elements.

Generalising the opinions expressed by various authors, we can accept the view that the nature of the interaction of metals with each other and with metalloids is very largely determined by the following factors: (1) the atomic radii; (2) the position in the electronegativity series of the elements; (3) the valency and ionisation potential.

None of these factors, taken in isolation, can explain the nature of the reactivity of metals. Correct conclusions can only be reached by considering them as interrelated factors.

### Atomic Radii

Many reactions between metals differ from normal chemical reactions (such as ionic, molecular, etc.) by having an atomic mechanism and by forming solutions and compounds in which the bond between the atoms is typically metallic. From this point of view, interatomic distances (which are determined by the atomic radii of the elements) acquire a special significance.

Atomic radii, like many other properties of the elements, exhibit a strong periodicity when plotted against atomic number. Atomic radii are shown in Fig. 1. In contrast to earlier methods of presentation by periods, the atomic radii are arranged by groups of the Periodic Table. In this scheme, the elements beryllium, boron, and aluminium are assigned to the B subgroups of second and third Groups II and III, because this provides greater continuity of the atomic radii than the alternative assignment to the A subgroups.

Nekrasov's "Course of General Chemistry"[30] mentions further examples of the similarity in chemical properties between beryllium and the metals of the zinc subgroup and aluminium. Also in the electronegativity series of the elements, beryllium is adjacent to the metals of subgroup IIB (see below).

As regards atomic radii, all the elements can be classified into three families: one includes the elements of moderately high atomic radius, the other two families include the elements at either extreme of the range of atomic radii.

Inspection of Fig. 1 shows the following characteristic features: the largest atomic radii are found with the metals of low atomic number of subgroups IA and IIA, that is, the most typically metallic elements; the smallest radii apply to the typical metalloids — B, C, N, O, H — found in the B subgroups of Groups III–VII. Within this series of elements the atomic radius decreases continuously from B to H. Heavy metals (of high atomic number) in those groups, such as In, Tl, Sn, Pb, Sb, Bi, Te, and Po, also show an increase in atomic radius with increasing atomic number. Metals belonging to transition groups (from III to VIII) and having unfilled *d*-electron shells, and also metals of Groups I and II (subgroup B) have intermediate values of the atomic radius, and most of them belong to the first family.

Within any one group, the atomic radius of the elements changes in the sense of continuous decrease with decrease in atomic number. Very closely similar elements, such as Ti, Zr, Hf; V, Nb, Ta; Mo, W; Fe, Co, Ni; Ag, Cu; and others, have very similar atomic radii.

The similarity (or the difference) in atomic radii of the elements, in conjunction with other properties of the reacting atoms, exerts a decisive influence on the interaction between metals, particularly as regards the formation of solid solutions.

### Position in the Electronegativity Series of the Elements

The second factor which determines whether a reaction of metallic character is possible is the position of the metals in the electronegativity series of the elements. In spite of the great importance of this factor in chemical reactions[31-37], its application to metal chemistry has attracted little attention. The concept of electronegativity[31,34,36]

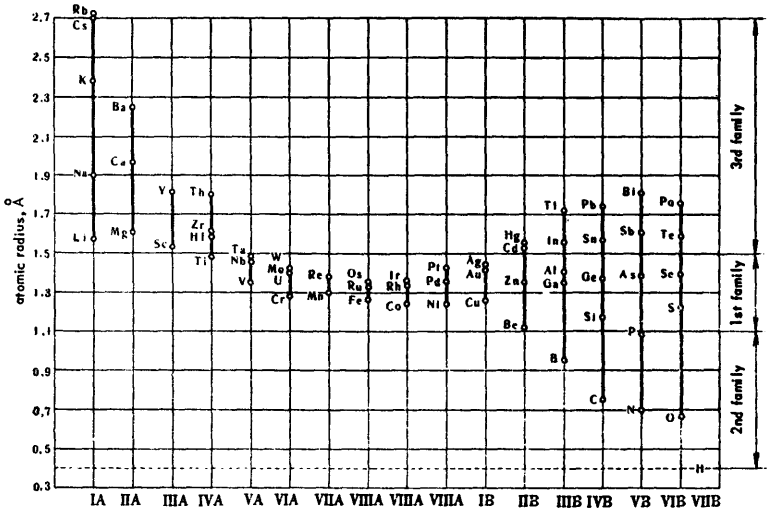



Fig.1. Variation of the atomic radii of the elements with their position in the groups of the Periodic Table.

embraces all the properties of an element stemming from the behaviour of the outer electrons of the atom. As a rule an element is electropositive if it shows a predominant tendency to give up electrons, and it is electronegative if its electron affinity is greater. The electronegativity difference between atoms A and B during formation of a chemical bond can be identified with the extent of electron transfer from atom A to atom B. The theory of this process is discussed in a number of monographs and reviews [31-35]: the conclusion is that metals are the most electropositive elements, and non-metals the most electronegative.

The electronegativity of the elements is arranged in an arbitrary series such that each element is electropositive with respect to the following element and electronegative with respect to the preceding element. In accordance with the project on the nomenclature of inorganic compounds set up by the Commission on the Nomenclature of Chemical Compounds, of the Division of Chemical Sciences of the Academy of Sciences of the USSR[36], the arbitrary electronegativity series for metals and non-metals is reproduced in Table 1.

It can be seen from Table 1 that the most electropositive metals are those of the alkali and alkaline earth series (with the exception of beryllium), whilst the metals of the B subgroups and beryllium are the most electronegative. These groups of metals are separated by braces in the table. Thus, as we have already pointed out, beryllium is situated close to aluminium from the standpoint of this important chemical property, and its behaviour towards other metals resembles that of aluminium rather than that of magnesium.

The transition group metals are situated between these two extreme poles corresponding to the electropositive and the electronegative metals. This series begins with actinium and ends with nickel, the most electronegative element of this group. In Table 1, the transition group is also separated from the other groups by a brace.

With very few exceptions, the electronegativity of metals within a group increases from bottom to top (see Table 1) with decreasing atomic number: for example U–W–Mo–Cr, etc. The exceptions are lithium, magnesium, beryllium, and tin, which occupy more electronegative positions than their analogues. The non-metals, bracketed together at the bottom of the table, show large deviations from electronegativity sequence within a group.

TABLE 1. Electronegativity series of the elements.

| | |
|---|---|
| Fr—Cs—Rb—K—Na<br>Ra—Ba—Sr—Ca—Li—Mg | electropositive metals |
| Ac—La—lanthanides—Y<br>Sc—Th—Hf—Zr—Ti<br>Pa—Ta—Nb—V<br>U—W—Mo—Cr<br>Re—Os—Ir—Pt<br>Tc—Ru—Rh—Pd<br>Mn—Fe—Co—Ni | transition group metals |
| Au—Ag—Cu—Hg—Cd—Zn<br>Tl—Pb—In—Ga—Al—Be<br>Bi—Sn—Sb—Ge | electronegative metals |
| Si—B—Te—As—P—C—H—At →<br>← Se—S—N—Br—Cl—O—F | non-metals |

The position of an element in the electronegativity series plays two important roles: it establishes the cause of the formation of solid solutions and intermetallic compounds and it explains the gradual transition from metallic compounds through covalent compounds to ionic compounds. The arbitrary electronegativity series of the elements helps to systematise the designation of intermetallic compounds.

In naming inorganic compounds, the most electropositive metal should be taken to be the electropositive part of the compound, and all the other elements present should be taken to be the electronegative part according to their position in the electronegativity series. As proposed by the above-mentioned Commission[36], the electropositive metal is written first in the formula of the compound. This basis of classification can also be used for naming intermetallic compounds†.

† The order in Table 1 is not that given in the 1957 IUPAC rules (Ed. of Translation).

The order in which the elements of ternary and more complex intermetallic compounds are written is the following: the most electropositive metal is written first in the formula, followed by the other elements in order of decreasing electropositivity. By analogy with Kurnakov's terms "metallic compounds" or "metallides", we may use the terms aluminides, beryllides, borides, carbides, nitrides, etc. All such generic names for intermetallic compounds are derived from the name of the electronegative elements present in the compounds.

## Valency and Ionisation Potential

The main factor which controls chemical reactions between elements is, of course, their valency.

The number of valency or outer electrons frequently ensures that the atoms in the resulting chemical compounds are present in stoichiometric ratios.

The number of valency electrons in interacting metals, and their quantum state, play an important part in determining the limiting concentrations of solid solutions and the composition of intermetallic compounds. The valency of the elements, like the properties discussed above, depends on their position in the Periodic Table. The most electropositive metals (Group I) have one outer electron; the number of these electrons increases as the number of the group increases, to six for metals and to seven for non-metals.

The increase in the number of outer electrons and in the interatomic binding force is reflected by a decrease in interatomic distance and in other properties of the metals, which show a gradual increase in density, in melting point, in hardness, in yield point, in elastic modulus, and a decrease in compressibility coefficient.

The binding force of electrons within the atom is determined by the ionisation potential, which is measured by the energy required to remove the outer (valency) electrons from the atom[31-34].

The first ionisation potentials of the elements of the Periodic Table are reproduced in Fig. 2 (after Vedeneev *et al.*[34]). Again, they are arranged in groups rather than by atomic number. From these data we can say that the most electropositive metals (Group I) have the lowest ionisation potentials, and that the ionisation potential increases with increasing group number: this is evident from Fig. 2. Another characteristic feature is that the transition group metals show very small differences in electronegativity irrespective of the number of outer electrons. This is a very significant factor in the formation of a wide class of solid solutions based on these metals.

With certain exceptions, the ionisation potential decreases within a group as the atomic number of the element increases. Metallic elements differ from non-metals in having lower ionisation potentials: this is particularly striking with elements of one and the same group. Thus, the ionisation potential of Group IVB elements, with the same number of outer electrons, drops sharply on going from C to Si, and more gradually on going from Si towards the more metallic elements Ge, Sn, and Pb (see Fig. 2). The ionisation potentials of the Group VB elements cover a wider range, that of nitrogen being highest, those of phosphorus and arsenic also quite high, and similar, and those of antimony and bismuth not far from the values

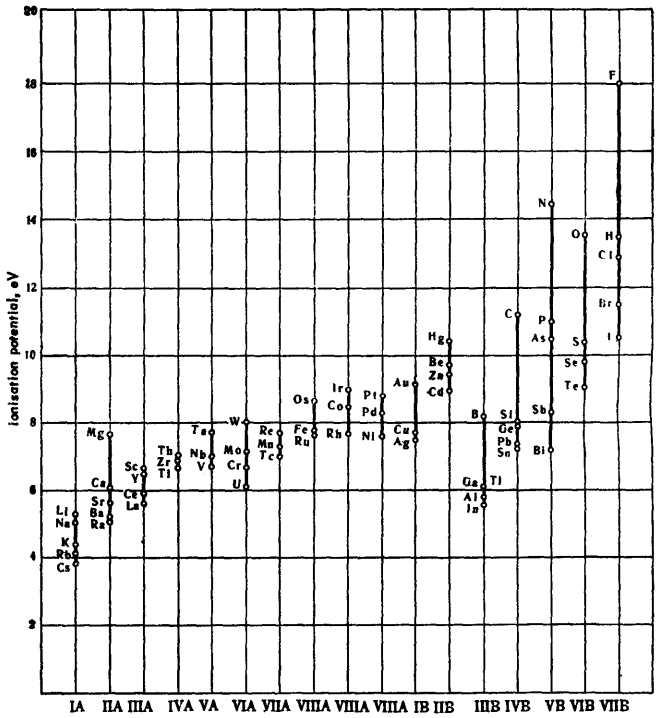



Fig. 2. Ionisation potential (first) of the elements arranged in groups of the Periodic Table.

typical of metals. Hence we can say that metals of low ionisation potential tend to give up their outer electrons during ordinary chemical reactions, whereas non-metals (large ionisation potential) readily accept electrons. Accordingly, reactions between metals and non-metals will produce compounds of ionic bond type.

Metal chemical reactions, in contrast to ordinary chemical reactions, show a characteristic tendency to form crystalline phases in which the electrons reside in the interionic regions, and can move with relative ease. This peculiarity of the collective distribution of valency electrons in the crystal lattice of complex metallic substances, without directional bonds, is highly typical of many metallic solutions and compounds. As a consequence, many products of metal chemical reactions have the metallic type of chemical bond.

By studying the physicochemical nature of metallic solid solutions, and the transition from solid solutions to compounds, it is easy to demonstrate a gradual change in chemical bond type and to relate it to the respective positions of the constituent elements in the Periodic Table. The wide spectrum of bond types observed in the products of reactions between metals, varying from purely metallic to ionic, demonstrates the fundamental status of the Periodic Law in the theory of metallic alloys.

## 4. FORMATION OF SOLID SOLUTIONS OF METALS

The term solid solutions (literally, "solidified solutions") first appeared in the literature in a report by Matthiessen[6], who studied the electrical conductivity of alloys as a function of composition, and was able to distinguish chemical

compounds, "solidified solutions", and mechanical mixtures of two metals from the shape of the "composition–property" curves. Following the development of the theory of phase equilibria, the concept of solid solutions achieved a wider significance, and was extended to include all solid phases of variable composition: isomorphous mixtures of metals, silicates, and other inorganic and organic systems. Thus, its influence has spread to all the fundamental types of equilibrium diagram for chemical systems[9,14,15,38,39].

The discovery of X-rays and their application to the study of the crystal structure of matter has made possible further developments in the theory of the formation of metal solid solutions. The conditions leading to the formation of solid solutions could be explained on the basis of ideas regarding the crystal lattice, the way in which atoms are located at crystal lattice sites, and data on interatomic distances in crystals. Metallic solid solutions (phases of variable composition) are formed either by replacing solvent atoms by solute atoms in the crystal lattice or by introducing solute atoms into the interstices of the solvent lattice. Thus, we now refer to two types of solid solution: 1) substitutional solid solutions, 2) interstitial solid solutions.

The fullest review of the historical developments in the science of solid solutions, of the theory of their formation, and of problems of chemical binding in metallic solid solutions is contained in the papers presented to the All-Union Conference on Solid Solutions, organised by the Division of Chemical Sciences and by the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR [39,40] in 1944.

Many theoretical approaches to the nature and properties of metallic solid solutions were considered at that conference. Substitutional solutions are treated as solutions or as the chemical replacement of metal atoms in the solvent metal lattice by foreign atoms (S. T. Konobeevskii), and it is shown that the formation of all metallic solid solutions is accompanied by a positive thermal effect, arising from the formation of chemical bonds between solvent and solute atoms. Dorfman concludes[40], from a study of various nickel solid solutions, that a rudimentary form of valence bond between atoms of the solvent and of the alloying element is present.

Thus, solid solutions are described as phases of variable composition with a single type of chemical bond. Under certain conditions, chemical reactions can occur in a uniform medium of these solutions: they take the form of ordered distributions of atoms and of singularities and extrema in the physicochemical properties on the composition–property diagrams.

Many theoretical problems in the chemistry of metallic solutions and of reactions occurring in such media (for example, heterogeneities in solid solutions and the formation of various compounds with a special type of bond between the electrons of the different atoms) have great scientific interest. These problems are discussed in a special monograph by Grum-Grzhimailo[41].

From the chemical point of view, problems such as the electronic structure of solid solutions, the theoretical model of the structure of solid solutions (Friedel *et al.*), atomic radii and distortions of the crystal lattice, lattice structure and lattice defects in solid solutions, are equally important. These problems are of immediate relevance to the departures of real solid solution systems from the ideal conditions of homogeneity and stability. Departures of this type are symptomatic of chemical reactions between the dissolved atoms.

Modern researches on the physicochemical nature of solid solutions confirm that the theory of metallic solid solutions is based on the electronic theory of metals[43]. The basic postulate of this theory is that the atoms of solid solutions are randomly distributed in the lattice, and that the electrons are distributed (as in the case of pure metals) in the interstices between lattice ions, without any directional bonds. This model of the atoms and electrons of the solvent and solute metals presupposes the existence in the lattice of solid solutions of ionised atoms, with a collective distribution of quasi-free electrons. However, the possibility of interactions between the electrons of different atoms cannot be excluded, since atoms of different kinds are present in such a lattice[41,42].

The presence of chemical binding of this type in solid solutions manifests itself in changes in the thermochemical, physical, and other properties of systems consisting of solid solutions. These changes cannot be easily explained by simple geometrical considerations of substitutional or interstitial foreign atoms in the lattice of the solvent metal, without allowance for the chemical interaction between the electrons of the different atoms in solid solution lattices.

The number of valency electrons involved, and the extent to which they interact, control the conditions of formation of solid solutions, the degree of distortion of the crystal lattice, and the degree of disorder in the distribution of the atoms over the solid solution lattice. As we shall show below, these same factors determine the change from solid solutions to intermetallic compounds.

We shall now discuss the basic factors which control the conditions of formation of metallic solid solutions.

The most general and most important factor, as Ageev correctly points out[43], is the position of the elements in the Periodic Table, since this determines the electronic structure of the interacting atoms. From this fundamental factor stem derived criteria, which determine the conditions most favourable to the formation of a continuous series of solid solutions. These are: (1) not too large a difference in atomic radii and in electronegativity and ionisation potential — as was pointed out in the previous Sections, this criterion is met mainly by metals which are analogues or which occupy neighbouring positions in the Periodic Table; (2) if all these parameters have reasonably similar values, a continuous series of solid solutions is formed provided that the atomic radii do not differ by more than 8–10%. The conditions most conducive to the formation of a continuous series of solid solutions are that the metals should belong to the same group and have the same number of valency electrons, and that they should be capable of crystallising in isomorphous lattices.

If the difference between the atomic radii of the metals is increased from 10 to 16%, if their position in the electronegativity series is changed, or if the number of valency electrons is varied, the tendency to form solid solutions decreases. When the difference between the atomic radii exceeds 16%, and the difference in electronegativity and ionisation potential is large, there is a sharp drop in the tendency to form solid solutions, and when the difference exceeds 20% not only are solid solutions not formed, but the metals are immiscible even in the molten state.

This relation between atomic radii and the ability to form solid solutions can be explained by assuming that the

crystal lattice of the solvent metal can accommodate a certain amount of distortion when solvent atoms are replaced by solute atoms. Evidently, there is a maximum degree of lattice distortion beyond which the lattice has no stable existence. The writer has discussed these problems in the particular case of iron solid solutions[44]. Fig. 3 shows the distribution of atoms in the $\alpha$-Fe body-centred cubic lattice, both without lattice distortion (Fig. 3*a*) and with lattice distortion due to a 15% difference in atomic radius between a solute atom and iron (Fig. 3*b*). It is easy to see, by comparing Figs. 3*a* and 3*b*, that the solvent lattice becomes deformed when this difference ($dr$) increases: as long as the atomic radius difference is no more than 8–10%, atoms can be replaced indefinitely without destroying the stability of the lattice, but for larger radius differences (15% and over), and larger degrees of lattice distortion, solvent atoms can be replaced only up to a definite concentration at which the solubility limit is reached and a new phase of different crystal lattice type is formed. Analogous effects have also been reported by other workers[20,41] in the formation of solid solutions with various interatomic radii.

This treatment of the conditions under which solid solutions will form, being primarily based on the size-factor, is not comprehensive and should be coupled with the behaviour of the valency electrons and their interactions in the lattice of solid solutions.

The criteria for the formation of a continuous series of solid solutions listed above are most nearly satisfied by transition group metals with an unfilled *d*-electron shell, showing the greatest similarity in atomic radii and chemical properties (see Figs. 1 and 2). Many metals of these groups will give continuous solid solutions both within their group of the Periodic Table (same number of outer electrons) and with metals of adjacent groups (small difference in the number of valency electrons). Examples of this are the interactions between metals of the following groups: Group IV Ti, Zr, Hf; Group V V, Nb, Ta; Group VI Cr, Mo, W; Group VIII Fe, Co, Ni (iron subgroup) and Pd, Pt, Ir (platinum subgroup), and others. Metals crystallising in different lattice types are the only exceptions.

All the analogue-metals of the above triads form continuous series of solid solutions with one another. Continuous solid solubility for many of these systems was predicted by the writer[44] and confirmed by later work[45]. The formation of continuous series of solid solutions by metals of the transition groups also shows some regularity along horizontal rows, as evidenced by the systems Ti–V, Ti–Cr, Zr–Nb, Nb–Mo, Nb–W, etc.

The maximal number of systems of this type was calculated, according to the crystal lattice type, for three

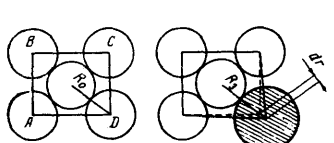



Fig. 3. Arrangement of atoms in the $\alpha$-Fe lattice (body-centred cubic) and in derived solid solutions:
*a*) in the $\alpha$-Fe lattice;
*b*) after substitution of an atom with 15% difference in radius.

classes of continuous solid solutions: (1) face-centred cubic lattice ($\gamma$-Fe); (2) body-centred cubic lattice ($\alpha$-Fe); (3) hexagonal lattice ($\alpha$-Ti).

Systems with continuous solid solutions between transition group metals of these three classes are listed in Table 2, which shows that metals which are nearest analogues can give continuous solid solutions even when the difference in atomic radii is as high as 10–11% (Ni–Rh, Ni–Ir, and some others). This is an example of the position of the elements in the Periodic Table and the similarity in chemical properties having a decisive effect on the nature of the interaction.

These metallic systems had not been investigated prior to the writer's publication[44], and the continuity of the solid solutions was then only tentatively predicted. Many of the systems have now been experimentally investigated, and it has been shown that the solid solutions are indeed continuous[45].

The systems with continuous solid solubility listed in Table 2 include the most refractory metals. Some typical fusion diagrams for these systems are shown in Fig. 4. As an example, we have reproduced the diagrams for systems with the $\gamma$-Fe lattice (Fe–Ni, Pt–Ir), the $\alpha$-Fe lattice (Fe–Cr, Cr–Mo, Cr–W, etc.), and the $\alpha$-Ti lattice (Ti–Zr, Zr–Hr, Ru–Os).

The tendency to form continuous solid solutions within a group of elements is also shown by groups other than the transition metals within which the difference in atomic radii is small and the electronic structure of the atoms is similar. This rule applies equally to highly electropositive and highly electronegative metals, including also some metalloids.

For example, among the electropositive metals, pairs such as K and Rb, Rb and Cs, Ca and Sr, Ca and Ba, and Ba and Sr, and among the electronegative elements Ge and Si, Bi and Sb, and Sb and As, have closely similar atomic radii and other properties (see Figs. 1 and 2), and

TABLE 2.

| Binary metal systems | Atomic diameters of the metals (Å) and difference in diameter, % | | | Binary metal systems | Atomic diameters of the metals (Å) and difference in diameter, % | | |
|---|---|---|---|---|---|---|---|
| | I | II | difference | | I | II | difference |
| **Continuous solid solutions of metals with the $\gamma$-Fe lattice in the systems:** | | | | **Continuous solid solutions of metals with the $\alpha$-Fe lattice in the systems:** | | | |
| $\gamma$-Fe—Ni | 2.52 | 2.49 | 1.2 | $\alpha$-Fe—Cr | 2.54 | 2.57 | 1.2 |
| $\gamma$-Fe—$\beta$-Co | 2.52 | 2.50 | 0.8 | $\alpha$-Fe—V | 2.54 | 2.69 | 5.9 |
| $\gamma$-Fe—Rh | 2.52 | 2.68 | 6.3 | Cr—Mo | 2.57 | 2.80 | 8.9 |
| $\gamma$-Fe—Pd | 2.52 | 2.74 | 8.7 | Cr—W | 2.57 | 2.82 | 9.7 |
| $\gamma$-Fe—Ir | 2.52 | 2.71 | 7.6 | Cr—V | 2.57 | 2.69 | 4.7 |
| $\gamma$-Fe—Pt | 2.52 | 2.77 | 9.9 | Mo—W | 2.80 | 2.82 | 0.7 |
| $\beta$-Co—Ni | 2.50 | 2.49 | 0.4 | Mo—V | 2.80 | 2.69 | 4.1 |
| $\beta$-Co—Rh | 2.50 | 2.68 | 7.2 | Mo—Nb | 2.80 | 2.94 | 5.0 |
| $\beta$-Co—Pd | 2.50 | 2.74 | 9.6 | Mo—Ta | 2.80 | 7.94 | 5.0 |
| $\beta$-Co—Ir | 2.50 | 2.71 | 8.4 | W—V | 2.82 | 2.69 | 4.8 |
| $\beta$-Co—Pt | 2.50 | 2.77 | 10.8 | W—Nb | 2.82 | 2.94 | 4.3 |
| Ni—Rh | 2.49 | 2.68 | 7.6 | W—Ta | 2.82 | 2.94 | 4.3 |
| Ni—Pd | 2.49 | 2.74 | 10.0 | V—Nb | 2.69 | 2.94 | 9.3 |
| Ni—Ir | 2.49 | 2.71 | 8.8 | V—Ta | 2.69 | 2.94 | 9.3 |
| Ni—Pt | 2.49 | 2.77 | 11.2 | Nb—Ta | 2.94 | 2.94 | 0.0 |
| Rh—Pd | 2.68 | 2.74 | 2.2 | **Continuous solid solutions of metals with the $\alpha$-Ti lattice in the systems:** | | | |
| Rh—Ir | 2.68 | 2.71 | 1.1 | | | | |
| Rh—Pt | 2.68 | 2.77 | 3.3 | $\beta$-Ti—$\beta$-Sc | 2.93 | 3.28 | 9.3 |
| Pd—Ir | 2.74 | 2.71 | 1.1 | $\alpha$- and $\beta$-Ti—$\alpha$- and $\beta$-Zr | 2.93 | 3.19 | 8.9 |
| Pd—Pt | 2.74 | 2.77 | 1.1 | $\alpha$- and $\beta$-Ti—$\alpha$- and $\beta$-Hf | 2.93 | 3.17 | 8.2 |
| Ir—Pt | 2.71 | 2.77 | 2.2 | $\alpha$- and $\beta$-Zr—$\alpha$- and $\beta$-Hf | 3.19 | 3.28 | 0.6 |
| | | | | $\beta$-Zr—$\beta$-Sc | 3.19 | 3.28 | 5.6 |
| | | | | $\beta$-Hf—$\beta$-Sc | 3.17 | 3.02 | 5.0 |
| | | | | Os—Ru | 2.68 | 2.70 | 0.8 |
| | | | | Os—Re | 2.68 | 2.75 | 2.6 |
| | | | | Ru—Re | 2.70 | 2.75 | 1.9 |

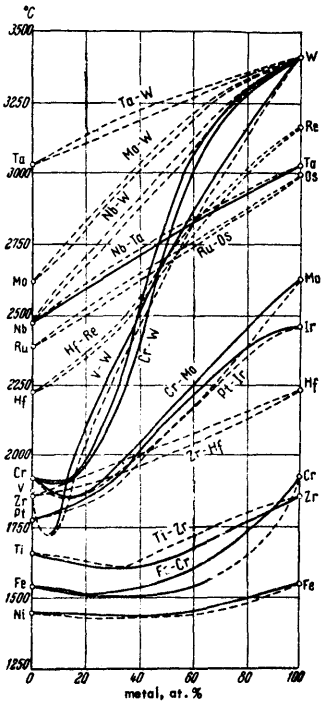



Fig.4. Fusion diagrams of systems of transition group metals forming continuous solid solutions.

form continuous solid solutions[45]. The mutual replacement of germanium and silicon, or antimony and arsenic atoms in the crystal lattice of these substances depends on the closeness of the atomic radii, on the equality of the number of valency electrons, and on the identity of crystal types. It is characteristic of these systems that germanium and silicon, being nearest analogues, can form continuous solid solutions in spite of the fact that one of them is a metal and the other a typical non-metal.

However, if the difference in atomic radii and in ionisation potential and electronegativity is large for elements of a given group (for example, C and Si, Bi and As), solid solutions cannot be formed, even though the number of valency electrons is the same[45].

The tendency towards restricted solid solubility in systems increases as we go from metal analogues to metals belonging to different groups, with different metal chemical properties (atomic radii, electronegativities, and number of valency electrons).

Thus, the tendency of a given metal (from Group VIII, say) to form solid solutions with metals of the Fourth Period decreases from right to left, whilst the opposite is true for a Group IV metal, the tendency decreasing from left to right. This can be illustrated by taking Ni (Group VIII) and Ti (Group IV) as examples.

The solubility of metals in nickel decreases in the following sequence:

| | Ni → Co → Fe → Mn → Cr → V → Ti → Sc → Ca → K | | | | | | |
|---|---|---|---|---|---|---|---|
| Solubility, at. % | 100 | 100 | 100 | 50 | 43 | 15 | unknown—insoluble. |

Nickel forms continuous solid solutions with the series from Co to Mn; from Cr to Sc only restricted solid solutions are formed, the solubility decreasing from Cr toward Ti and Sc, and with Ca and K there is practically no interaction. This is exactly what would be expected from the similarities and the differences in metal chemical properties between these metals and nickel. With titanium — a Group IV metal — the situation is reversed. The solubility of elements in β-titanium decreases in the sequence

| | V → Cr → Mn → Fe → Co → Ni | | | | | |
|---|---|---|---|---|---|---|
| Solubility, in Ti, at. % | 100 | 100 | 28 | 20 | 13 | 10 |

The β modification of titanium forms continuous solid solutions with V and Cr, but it forms only restricted solid solutions with Mn, Fe, Co, and Ni. It is clear from the solubility series that the maximum concentration of metals having a restricted solubility in β-titanium also decreases progressively from manganese towards nickel, that is, as the difference in metal chemical properties between these metals and titanium increases.

The systems formed by the β modification of titanium with the series of elements from Cr to Ni are illustrated in Fig. 5. Whereas Cr has an unrestricted solubility in β-titanium, the solubility of the other metals at their eutectic temperature decreases continuously in the sequence Mn → Fe → Co → Ni. The crystallisation temperature of the eutectic also decreases accordingly in these systems. The strictly sequential decrease in solubility in β-titanium of the series Mn → Fe → Co → Ni corresponds to the increasing separation of these elements of the Fourth Period from the position occupied by titanium, to a gradual increase in the number of electrons in the unfilled *d* shell, and to an increasing difference in atomic radii between titanium and these elements. These regular changes in limiting solubility can be demonstrated with many other metals.

Thus, starting from the fundamental physicochemical factors which determine the type of interaction between metals, the formation of solid solutions can be similarly classified for a number of metals of the Periodic Table. This has been done for silver and copper[20], magnesium and aluminium[46,47], iron and nickel[46,48], and chromium and

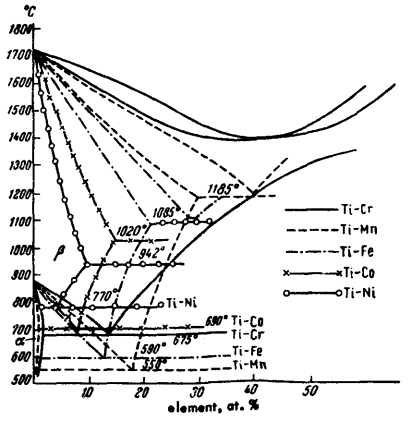



Fig.5. Fusion and solubility diagrams for the systems formed by β-Ti with Cr, Mn, Fe, Co, and Ni.

titanium[49,50]. The solubility of various elements in manganese[51] has been discussed recently, as well as more general aspects of the metal chemistry of niobium and vanadium, including the problem of the solubility of elements in these metals[52,53].

A knowledge of the mutual solubility of metals in binary systems is valuable in studies of the equilibria in multicomponent metallic systems with solid solutions. The limiting concentrations of alloys in multicomponent systems can be calculated from data on the behaviour of metals in binary systems, and complex solid solution compositions can be made. Calculations of this type were made by the writer for the production of 4-, 6-, 15-, and 16-component solid solutions based on nickel[54] and of 5-, 9-, and 10-component solid solutions based on $\alpha$-titanium.[55] These complicated solid solutions have many properties which are superior to those of pure metals and binary solid solutions. The preparation of these multicomponent solid solutions and the study of their properties are therefore of great theoretical and practical interest.

## 5. FORMATION OF INTERMETALLIC COMPOUNDS

The formation of various types of compound by metals with other metals or with non-metals is one of the characteristic reactions of metal chemistry. The products of such reactions have been termed intermetallic compounds or metallides[8]. This term applies to all the compounds formed between metals, whether their bond type is metallic or covalent. In addition to the reviews already mentioned[24-29], many investigations have been concerned with the formation, classification, and structure of intermetallic compounds, and have surveyed work in progress[56-61].

On the basis of the general principles for the classification of chemical compounds put forward by Kurnakov[8,14,15], intermetallic compounds can be subdivided into two main types: (1) compounds of variable composition (or berthollides), and (2) compounds of fixed composition (or daltonides).

These two types of intermetallic compounds are now generally accepted, and the terms are widely used in inorganic chemistry, metallography, and metal physics. They include not only the intermetallic compounds formed by crystallisation from molten alloys but also the compounds formed by transformations from solid solutions (see below). Among the berthollides and daltonides are included the many compounds formed by metals with non-metals of small atomic radius, such as carbon, nitrogen, oxygen, and hydrogen, and also the compounds with covalent bond type and semiconductor properties. Many compounds called carbides, nitrides, and sometimes suboxides and hydrides are in fact interstitial phases and have typically metallic properties.

The classification of high-melting compounds has been critically discussed[62] for a wide variety of compounds (mostly intermetallic compounds of the transition metals). The compounds were assigned to the following three classes: (1) compounds of two metals (true intermetallic compounds); (2) metal-like compounds (carbides, nitrides, phosphides, etc.); (3) compounds of two non-metals (non-metallic compounds between boron and carbon, carbon and silicon, etc.).

There is also a classification based on the regular changes in chemical bond character associated with the position of the elements in the Periodic Table. The first class includes the compounds formed by metals with other metals, that is, the true intermetallic compounds, such as beryllides, aluminides, stannides, antimonides, and many others. In the second class we find once again compounds with metallic bond type. The compounds of the first and the second class usually have a relatively simple crystal structure and belong to the cubic, the hexagonal, or the tetragonal system (close-packed atoms). All these compounds are studied in metal chemistry. Some of the compounds in the second class, composed predominantly of non-metal atoms, and the compounds formed by two non-metals, are non-metallic. Their chemical bond type is covalent or even ionic. Many have a complex crystalline structure and show semiconductor properties (high electrical resistance).

These compounds behave as independent components in equilibrium systems, and show distinctive singular points on composition–property diagrams (with the exception of the berthollides).

The singularity of properties is a characteristic criterion of compounds of fixed composition, whether formed by crystallisation from the melt or by transformations from solid solutions.

We will consider the metallic compounds formed as a result of decomposition of solid solutions. These compounds were first discovered (in 1914) by Kurnakov, during slow cooling of continuous solid solutions[56] in the Au–Cu system. The two compounds $AuCu_3$ and AuCu were identified in this way. Subsequently, compounds of this type were reported in many solid solutions, and called Kurnakov compounds in honour of their discoverer[26]. In contrast to solid solutions, all these compounds are characterised by an ordered distribution of atoms in their lattice.

At the present time, the systems giving continuous series of solid solutions without compound formation can be considered exceptional. Textbooks of physicochemical analysis[14,15], and many of the papers mentioned above[29], assign separate phases — corresponding to compounds on the equilibrium diagrams (see Fig. 6*a*) — to these metallic formations. These possess regions of homogeneity and the compositions of the compounds are distinguished by singular points. Compounds of this type are formed not only from continuous solid solutions, but also in systems with restricted solid solubility regions. Typical of these compounds are $VNi_3$, $VCo_3$, $MnAu_3$, $MgAg_3$, $Au_3Zn$, $Cu_3Zn$, $Fe_3Al$, and many others.

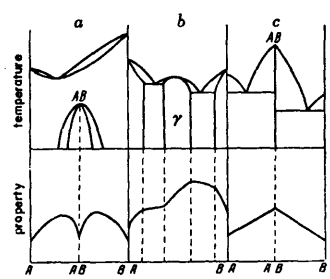



Fig. 6. Schematic equilibrium diagrams for metallic systems with three types of compound:
*a*) Kurnakov compound;
*b*) compound of the berthollide type;
*c*) compound of the daltonide type.

Among the recently discovered compounds are $Ti_6Al$ and $Ti_3Al$, formed from the restricted $\alpha$ solid solutions of aluminium in titanium[62]. Fig. 7, prepared from results obtained in the writer's laboratory, gives the equilibrium diagram of the system (above) and the variation of the Hall effect with alloy composition after long annealing (below). The compound $Ti_6Al$ is characterised by a break in the curve, whereas $Ti_3Al$ corresponds to the maximum at the intersection of two curves. The formation of this type of compound in the Ti–Al system causes marked changes in alloy properties; this has helped to clarify several anomalies in the mechanical and other properties of these alloys.

We have further developed Kurnakov's ideas regarding the importance of solid solutions in the formation of various types of compound, and have suggested that lower oxides of titanium can exist in the wide $\alpha$ solid solution region of the titanium–oxygen system. A detailed study of the alloys of the Ti–O system (up to 35 at.% oxygen) has recently provided experimental proof of the formation of the two previously unknown compounds $Ti_6O$ and $Ti_3O$ from titanium $\alpha$ solid solutions[63]. Both these compounds have metallic properties and crystallise with a hexagonal lattice, but $Ti_3O$ gives an X-ray pattern with superlattice lines which are characteristic of an ordered structure. The compounds $Ti_2O_3$ and $TiO_2$, which were previously known, belong to the valency type. The recently discovered compounds $Ti_6O$ and $Ti_3O$ can be classified as interstitial phases: they are still the only known examples of oxygen-containing compounds formed from restricted solid solutions. Because of these results, instead of the existing equilibrium diagram (Fig. 8) of the Ti–O system, showing a wide region of titanium $\alpha$ solid solutions, a new diagram was proposed[63], including the new compounds $Ti_6O$ and $Ti_3O$ (see Fig. 9). Analogous compounds of the suboxide type can be expected in other systems of chemically reactive metals with restricted oxygen solubility, for example, Zr–O, Hf–O, V–O, Nb–O, etc. A study of these systems would therefore be of interest.

The discovery of these compounds is very relevant to the understanding of the structure and physicochemical

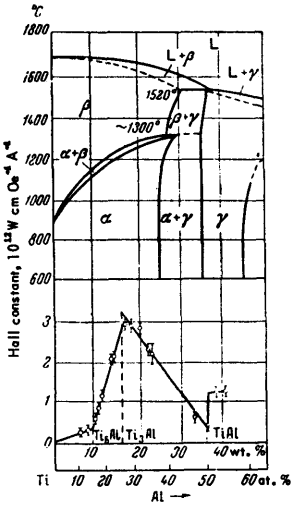



Fig. 7. Equilibrium diagram of the Al–Ti system and variation of Hall constant with composition.

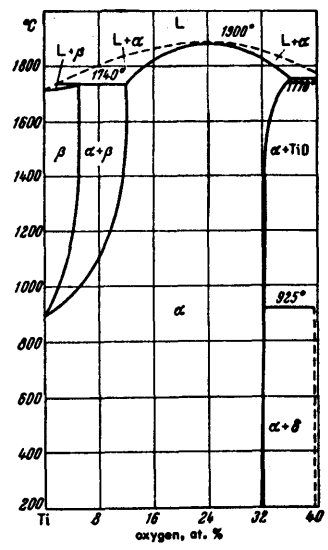



Fig. 8. Equilibrium diagram of the Ti–O system, showing wide field of titanium $\alpha$ solid solutions (from published data).

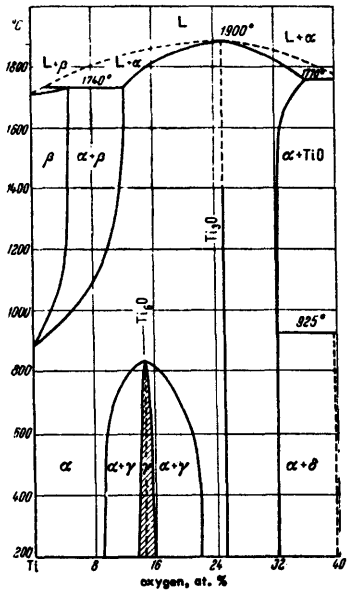



Fig. 9. Equilibrium diagram of the Ti–O system, showing the formation of the compounds $Ti_6O$ and $Ti_3O$ (from recent results).

properties of the alloys of titanium, zirconium, etc. which contain a high proportion of oxygen, and should help to throw light on the influence of oxygen on the mechanical and other properties of these metals.

The formation of intermetallic compounds and their relative stability depends on the difference in chemical properties (electronegativity, ionisation potential) of the interacting elements. The stability of intermetallic compounds

and the strength of their chemical bonds can be judged, as with any other chemical compound, by their heats of formation[64-66].

The available data show that the compounds between metal analogues, in which the difference in chemical properties between the two kinds of atom taking part in compound formation is smallest, are the least stable. In this sense, the least stable compounds are the Kurnakov compounds with an ordered structure, formed from solid solutions of analogue-metals. For example, the compound AuCu, mentioned above, has a heat of formation of 0.37 kcal × × mole$^{-1}$, whilst the compound FeCr, also formed from solid solutions, in the Fe–Cr system, has a heat of formation of 0.78 kcal mole$^{-1}$.

The author has made a study of the regularities displayed by the heats of formation of the intermetallic compounds of nickel of composition $MNi_3$, showing a gradual increase in the electronegativity difference between nickel and the metal M.

Fig. 10, prepared from the results of this work[67], shows the heats and temperatures of formation of the compounds of nickel with the following metals: Fe, Mn, Cr, V, and Ti, belonging to Groups VIII, VII, VI, V, and IV within the same period of the Periodic Table. As the difference in properties between nickel (electronegative) and the metals Fe, Mn, Cr, V, and Ti (electropositive) increases (see Table 1), the stability of the nickel compounds of composition $MNi_3$, involving these metals, increases in the sequence $FeNi_3 \rightarrow MnNi_3 \rightarrow CrNi_3 \rightarrow VNi_3 \rightarrow TiNi_3$.

The partly anomalous behaviour of the compound $CrNi_3$ in the above series calls for further examination. The first four compounds are formed from solid solutions and are therefore typical Kurnakov compounds, whereas $TiNi_3$, the most stable of the five, has the highest heat and temperature of formation and crystallises from the liquid phase. It should be noted that the difference in formation conditions (from the solid or the liquid phase respectively) has no effect on the gradual change in properties. This is proof of the generality of our proposition that the stability and the gradual changes in chemical bond strength of intermetallic compounds are a function of the position of the reacting elements in the Periodic Table.

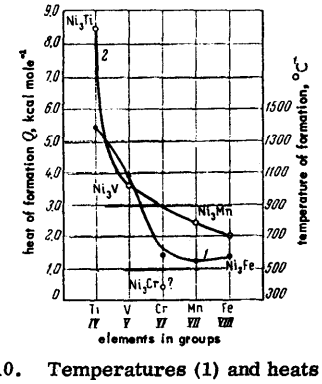



**Fig. 10.** Temperatures (1) and heats (2) of formation of compounds of nickel with iron, manganese, chromium, vanadium, and titanium of composition $MNi_3$.

We will now discuss some features of the formation of compounds of variable composition (the berthollides). They are characterised by the presence of a homogeneity region, and by the absence from the composition–property diagrams of well-defined singularities at the ordinates drawn through the composition of these compounds (see Fig. 6*b*). In the general classification of intermetallic compounds, berthollides are intermediate in stability between Kurnakov compounds and the compounds of the daltonide type. There are known examples of the formation of Kurnakov compounds from berthollide compounds stable at high temperatures when the temperature is lowered. A striking example of this is the transformation on cooling, in the Cu–Zn system, of the high-temperature $\beta$ phase of CuZn (berthollide) into the $\beta'$ phase (Kurnakov compound). The composition and crystal structure of these compounds is often determined by the ratio of the number of outer electrons to the number of atoms in the lattice of the compound. These compounds have been termed electron compounds; their quantum-mechanical theory is discussed in a number of papers[19,20,68]. Phases of this type are most readily formed by interaction between those metals of the B subgroups which are near neighbours in the Periodic Table and have a small electronegativity difference.

Isolated examples of the formation of such phases can be recognised in systems based on metals of Group I (Cu, Ag, Au) and metals of Groups II (Zn, Cd, Hg), III (Tl, In, Ga), V (Bi, Sb), and others. In some cases, the compounds under discussion are formed when these metals react with metals of the transition groups[46]. In the homogeneity region of these compounds, the properties change smoothly with composition, as shown in Fig. 6*b*.

With increasing difference in chemical properties between the reacting elements, associated with an increase in electronegativity difference, in the difference in ionisation potential, and in the difference in the number of valency electrons between the metals, the tendency to form intermetallic compounds of the second type (daltonides) increases. As shown in Fig. 6*c*, these are characterised by singularities in the composition–property diagrams.

This is particularly true of the interaction between the most electropositive metals of Groups I and II and the most electronegative metals of the B subgroups of Groups II–VI. This confirms Kurnakov's prediction[8] that the alkali and alkaline earth metals, being the main carriers of basic or metallic properties, should most readily form a variety of compounds with the heavy (and most electronegative) metals such as Hg, Zn, Cd, Pb, Sn, and Bi.

The gradual transition from metallic solutions through systems with berthollide compounds to intermetallic systems in which daltonides are formed can be demonstrated by selecting binary systems composed of analogue-metals and of metals differing in their chemical properties. Fig. 11, taken from Hansen and Anderko[45], shows three types of binary system: systems with continuous solid solutions of two nearest-analogue electropositive metals of Group I (K and Rb), restricted solid solutions based on metals and the berthollide $\omega$ phase in a system of two electronegative metals (Hg and Cd), and lastly a system in which no solid solutions are formed, but giving rise to six compounds of fixed composition (K, the most electropositive metal, and Hg, the most electronegative metal). All these compounds ($KHg_{11}$, $KHg_8$, $KHg_4$, $KHg_3$, $KHg_2$, and KHg) have higher melting points than their constituent metals: they are characterised by bonds of the metallic type and are typical intermetallic compounds.

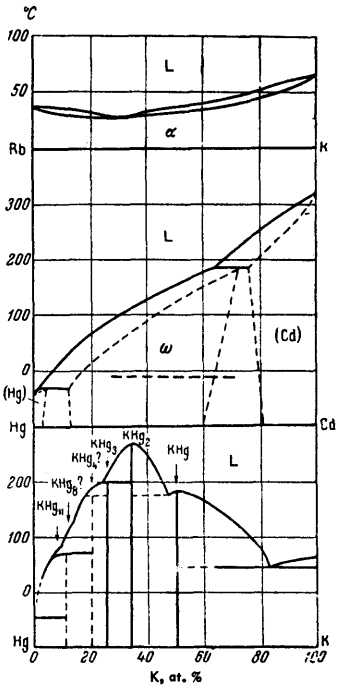



Fig. 11. Equilibrium diagrams of systems of two analogue-metals (K–Rb and Hg–Cd) and of metals from different subgroups (K–Hg).

On the other hand, compounds with different types of chemical bond are formed[31,65,66] in some metal–non-metal systems according to the concentration of the electronegative element. For example, in the series of compounds $Ti_6O$, $Ti_3O$, TiO, $Ti_2O_3$, and $TiO_2$ of the Ti–O system, the first two have metallic bonds, TiO has covalent bonds, and $Ti_2O_3$ and $TiO_2$ have predominantly ionic bonds.

Many compounds, for example, those formed by the electropositive metal magnesium with electronegative elements, show a characteristic transition from metallic to covalent and ionic bond character as the difference in chemical properties between the second component and magnesium is increased. This can be observed in the series of compounds formed by magnesium with the elements of Group IV (Pb, Sn, Ge, and Si). It should first be noted that all the compounds of magnesium with these elements correspond to the normal valency relationships: their composition is described in every case by the formula $Mg_2X$. As the electronegativity of the elements increases from Pb towards Si, transition from a purely metallic bond ($Mg_2Pb$) to a covalent bond takes place ($Mg_2Sn$, $Mg_2Ge$, $Mg_2Si$).

This same transition and gradual change in bond type is observed also in the series of compounds formed by magnesium with the elements of the Third Period: $Mg_3Al_2$, $Mg_2Si$, $Mg_3P_2$, MgS, and $MgCl_2$. These compounds also obey the valency rules, as their composition shows. The elements Al, Si, P, S, and Cl, present as a constituent, show increasing electronegativity and ionisation potential (see Table 1 and Fig. 2). Of these, only Al is a true metal, the remainder being non-metals. Although Al is situated in the Third Period close to Mg, it is quite unlike the electropositive element magnesium in its electronegativity (see Table 1). Hence, aluminium and magnesium form a series of compounds, including $Mg_3Al_2$, all of which are typically metallic. The next three compounds, $Mg_2Si$, $Mg_3P_2$, and MgS have covalent bonds and are semiconductors, possibly with partial ionic bond character. The last compound of this series, $MgCl_2$, is a typical compound with ionic bond character.

As the difference in chemical properties between magnesium and the above elements increases, whether along a group or along a period, the strength of the chemical bond of the magnesium compounds increases. This is reflected in an increase in the heat of formation and melting point of compounds of a given stoichiometric composition, as shown in Table 3.

The table lists the change in heat of formation ($Q$, kcal × × mole$^{-1}$) of compounds of magnesium with elements showing gradually increasing electronegativity difference with respect to magnesium.

A general survey of the heats of formation of compounds is sufficient to show that intermetallic compounds have much lower heats of formation than compounds of a covalent or ionic bond type. In all three columns of Table 3 the heat of formation increases from top to bottom, in the same sense as the electronegativity of the reacting elements: from Pb to Si for Group IV (B subgroup), from Te to O for Group VI (B subgroup), and from Si to Cl for the Third Period.

The stability of intermetallic compounds is also related to their melting point. The highest chemical bond strength corresponds, as a rule, to the highest melting point. This is illustrated by the linear plots of Fig. 12, which join the melting points of the compounds of Mg with Pb, Sn, Ge, and Si.

The melting points of the compounds $Mg_2Pb$, $Mg_2Sn$, $Mg_2Ge$, and $Mg_2Si$ show a gradual increase, corresponding to the tabulated heats of formation. For comparison, Fig. 12 also shows published values[45] of the melting point of compounds of lithium with lead and tin. These also show an increase in melting point on going from $Li_4Pb$ to $Li_4Sn$.

Linear extrapolation to the hypothetical compounds $Li_4Ge$ and $Li_4Si$, for which there are no published data, affords an estimate of their melting points (~870° for $Li_4Ge$ and ~980° for $Li_4Si$).

These regularities in the heats of formation and the melting points of intermetallic compounds, depending on the relative positions of the reactants in the Periodic Table, are expected to apply to many intermetallic and metal-like compounds. This can be demonstrated by inspection of a series of compounds between metals and metals or between metals and non-metals. Regularities of this type have been found in the gradual change in chemical bond type and heat of formation of borides[69], carbides[70], silicides[71],

TABLE 3. Heats of formation of compounds of magnesium with various elements.

| Compounds with Group IVB elements | $Q$, kcal mole$^{-1}$ | Compounds with Group VIB elements | $Q$, kcal mole$^{-1}$ | Compounds with elements of the Third Period | $Q$, kcal mole$^{-1}$ |
|---|---|---|---|---|---|
| $Mg_2Pb$ | 4.2 | MgTe | 25.0 | $Mg_2Si$ | 6.3 |
| $Mg_2Sn$ | 6.1 | MgSe | 30.0 | $Mg_3P_2$ | 25.6 |
| $Mg_2Ge$ | 6.1 | MgS | 42.2 | MgS | 42.2 |
| $Mg_2Si$ | 6.3 | MgO | 73.0 | $MgCl_2$ | 51.1 |

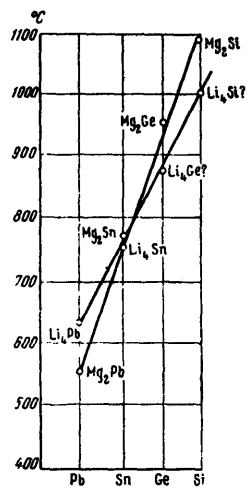



Fig. 12. Melting points of compounds of magnesium and lithium with Group IVB elements.

phosphides[72], and other compounds between metals and non-metals.

Tentative heats of formation[69-71] ($Q$, kcal mole$^{-1}$) of some borides and carbides of transition metals of Groups IV and V, of identical stoichiometry, are reproduced in Table 4. Although the data available for the borides of these metals are incomplete, we may conclude that the heats of formation increase in the same order as the electropositivity of the metal. The compounds formed between phosphorus and various metals are perhaps the most interesting from this point of view.

Starting from the fundamental properties of the phosphorus atom — larger atomic radius and lower electronegativity than its analogue, nitrogen — Samsonov and Vereikina point out[72] that the compounds of phosphorus with the transition metals cannot be regarded as interstitial phases except for the lanthanide phosphides. From electronegativity considerations, metal phosphides should have a much lower ionic bond character than nitrides, and their properties should be less metallic than those of arsenides, antimonides, and bismuthides. Phosphorus also gives intermetallic compounds more readily than does sulphur.

As the number of phosphorus atoms in transition metal phosphides decreases, the role of the M–P and P–P bonds becomes less important and the M–M bond becomes predominant. The properties of the phosphides, like those of the carbides and nitrides, become more metallic under these conditions.

TABLE 4. Heats of formation of some metal borides and carbides.

| Group | Borides | | Carbides | | Group | Borides | | Carbides | |
|---|---|---|---|---|---|---|---|---|---|
| | composition | $Q$, kcal × mole$^{-1}$ | composition | $Q$, kcal × mole$^{-1}$ | | composition | $Q$, kcal × mole$^{-1}$ | composition | $Q$, kcal × mole$^{-1}$ |
| IV | $TiB_2$ | 70.2 | TiC | 43.8 | V | $VB_2$ | — | VC | 30.2 |
| | $ZrB_2$ | 78.0 | ZrC | 44.4 | | $NbB_2$ | 36.0 | NbC | 33.6 |
| | $HfB_2$ | – | HfC | 81 | | $TaB_2$ | > 52 | TaC | 36.0 |

TABLE 5. Heats of formation of phosphides of the iron group.

| Compound | $Q$, kcal mole$^{-1}$ | Compound | $Q$, kcal mole$^{-1}$ | Compound | $Q$, kcal mole$^{-1}$ |
|---|---|---|---|---|---|
| $Fe_3P$ | 13.1 | $Co_2P$ | 28.45 | $Ni_5P_2$ | 17.4 |
| $Fe_2P$ | 19.25 | CoP | 34.0 | $Ni_2P$ | 19.2 |
| FeP | 29.0 | $CoP_3$ | 64.0 | $NiP_2$ | 38.0 |
| $FeP_2$ | 42.0 | | | $NiP_3$ | 45.2 |

In keeping with their greater percentage of metallic bond character, phosphides should have a lower heat of formation than nitrides. This is because the ionisation potential and electronegativity of the phosphorus atom are lower than those of the nitrogen atom. The transition from phosphides containing relatively few phosphorus atoms to phosphides containing more phosphorus atoms is accompanied by an increase in heat of formation ($Q$, kcal mole$^{-1}$), as shown[72] by the phosphides of iron, cobalt, and nickel listed in Table 5.

These data indicate that, as the number of phosphorus atoms in the compounds increases, so does the number of P–P and P–M bonds; as a result, covalent and ionic bonds begin to predominate. These raise the bond strength and bring about an increase in the heat of formation of the compounds.

Samsonov and Rodzinskaya[73] have demonstrated some measure of regularity in the chemical bond character of sulphides, related to the electronic structure of rare-earth elements and sulphur. They point out that "metallisation" of the bond occurs to a greater extent in sulphides than in the nitrides of the same metals, and ascribe this to the ionisation potential of sulphur, which, like that of phosphorus, arsenic, and carbon, is lower than the ionisation potential of nitrogen (see Fig. 2). Consequently, the sulphides of these metals (of given stoichiometric composition) can be expected to show greater collectivisation of the electrons from the metal and from the sulphur, and greater metallisation of the bond, than the corresponding nitrides. However, even the sulphides retain some covalent and ionic bond character: as in the phosphides, this increases with the number of sulphur atoms in the compound. For example thorium monosulphide ThS is a typical intermetallic compound[74], whereas $Th_2S_3$, $Th_4S_7$, and $ThS_2$ are classified among the compounds with a covalent and partially ionic bond.

This discussion of the influence of the physicochemical nature of the constituent atoms upon the nature of the chemical bond in intermetallic compounds demonstrates the importance of the metal chemical properties of the elements from the point of view of the formation of various types of compound. Many of the physical, mechanical, and other properties of these compounds are determined by the strength of the chemical bond.

## 6. CRYSTAL CHEMICAL REACTIONS IN METALLIC SYSTEMS

The study of crystal chemical reactions in metallic systems[28,74] is one of the main aspects of current work in the field of metal chemistry. The term includes a wide variety of reactions involved in phase transformations in

metallic systems and in surface reactions in the solid (crystalline) state. In contrast to the familiar chemical reactions in liquid and gaseous media, which usually occur by a homogeneous mechanism, these reactions are essentially heterogeneous and occur in a crystalline medium. We shall therefore call them crystal chemical reactions. Many of the problems involved are part of the general development of solid state chemistry.

Crystal chemical reactions include: (1) reactions leading to the formation of Kurnakov compounds from solid solutions; (2) reactions leading to the formation of compounds or other phases from supersaturated solid solutions; (3) eutectoid and peritectoid reactions; (4) surface reactions (oxidation, reduction, and other reactions in the solid state); (5) solid-phase reactions between powders of metals and non-metals.

Crystal chemical reactions are atomic rather than molecular in character[75]. They relate to the rearrangement and mutual replacement of atoms in a crystalline medium, and their rates are controlled by diffusion processes. The range of reaction times presented by these reactions is unusually wide: they vary from instantaneous reaction (in the case of martensitic transformations) to hundreds, thousands, or millions of hours, up to geological times (low-temperature decomposition of supersaturated solid solutions, etc.).

The rates of reactions in the solid state depend on a number of equilibrium considerations. Firstly, they depend on the chemical composition and crystal structure of the reaction medium, on the temperature, and on the pressure. These factors can accelerate or suppress the reaction rate. For example, it has been shown that individual chemical species involved in these processes correspond to singularities in the "composition–reaction time" diagrams. Hence, the author[76] has proposed a method of physicochemical analysis based on the effect of composition on the reaction time or the reaction rate in metallic systems. Studies of the reactivity of alloys (solid solutions, intermetallic compounds, heterogeneous alloys) are concerned with metal chemical reaction problems. Solid solutions and compounds can exhibit chemical passivation (the loss of reactivity at normal or elevated temperatures). Many corrosion-resistant and heat-resisting metallic materials have been developed on the basis of these properties. These are frequently homogeneous metallic solid solutions or intermetallic compounds. The chemical stability of these materials is hundreds of times greater than that of the starting components.

Crystal chemical reactions have one special feature in common: since they take place in the solid state, the intermediate states of reactions in progress may be "frozen" under various conditions, giving rise to a metastable structure of the resulting compounds or phases. Phases of this kind, being still in their formation stage, are dispersed in varying degrees: their atoms are not in their equilibrium crystal lattice sites. Due to their non-equilibrium state, these atoms are more reactive than the atoms of solid solutions and compounds in a state of equilibrium. This is strikingly confirmed by the high catalytic activity of many metastable states of metallic solid solutions and compounds[77].

A detailed characterisation of crystal chemical reactions and a substantially complete survey of the literature would go beyond the scope of the present review: there will be only a brief discussion of some types of crystal chemical reaction.

As was stated above, many solid solutions (both continuous and restricted) can undergo reactions with formation of Kurnakov compounds having, as a rule, a different type of crystal structure as compared with the solid solutions from which they are formed. The atoms have an ordered distribution in the lattice of these compounds, in contrast to the disordered structure of solid solutions. The compositions of these compounds can be recognised by singularities in the composition–property diagrams, and they extend over definite regions. The classical example of this type of equilibrium diagram arose from the experimental study[45,46] of the copper–gold system (see Fig. 13), showing the compounds $Cu_3Au$ and CuAu. Both these compounds, formed from solid solutions, are characterised by singular points on the plots of electrical resistivity and hardness against composition (Fig. 13).

Examples of the formation of Kurnakov compounds are very numerous[45]. At the moment, systems of solid solutions in which compounds of this type cannot be detected under suitable conditions are definitely exceptional.

Many restricted solid solutions in metallic systems show varying solubility in the solid state. As a rule, the solubility is highest at temperatures of transition from the solid to the liquid state (that is, at the solidus point), and decreases with decrease in temperature, as shown schematically by curves $SQ$ of Fig. 14*a*.

Because of this change in solubility, heat treatment — quenching the alloys from temperatures close to the solidus point — can be used to fix the solid solutions in a state of supersaturation for concentrations extending almost to the limiting solubility of the component at point $S$. The linear variation of lattice parameter with composition can be used to confirm that the solution is in a supersaturated condition, as shown in Fig. 14*b*. Under favourable conditions, decomposition of the supersaturated solid solution and precipitation of the phase in excess can occur in these metastable systems. This follows from thermodynamic considerations of the free energies of the phases in the

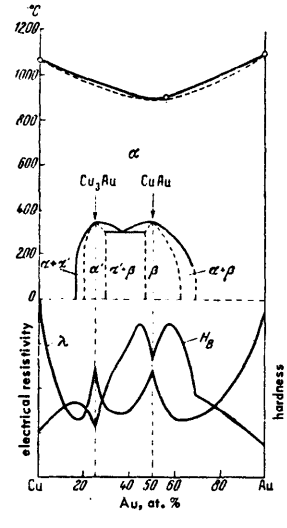



Fig. 13. Equilibrium diagram of the Au–Cu system, and change in electrical resistivity and hardness with alloy composition.

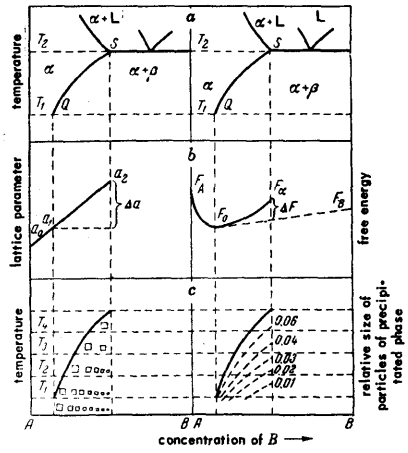



Fig. 14. Diagram showing changes in solubility (*a*), lattice parameter and free energy (*b*), and particle size of the precipitated phase formed by decomposition of supersaturated solid solutions (*c*).

equilibrium and the metastable states. The right-hand side of Fig. 14*b* shows the change in the free energy $F_A$ of the phase in equilibrium at temperature $T_1$. The minimum of the curve ($F_0$) corresponds to the equilibrium solubility limit, and its maximum ($F_\alpha$) to the non-equilibrium state of the $\alpha$ supersaturated solid solution. It follows that the supersaturated $\alpha$ solid solution must necessarily undergo transformation with formation of a precipitated phase in supersaturated (quenched) alloys lying to the right of the equilibrium solubility curve *SQ*. These decomposition reactions involve atomic rearrangements, the formation of intermediate, highly disperse phases, and the approach to and achievement of equilibrium phase structures. The grain size of the precipitated phases formed in these crystal chemical reactions depends on the composition, temperature, and time of the reaction.

The particles of the precipitated phase obtained in a fixed time at temperatures $T_1$, $T_2$, $T_3$, and $T_4$ are shown schematically in Fig. 14*c* as small squares (on the left) and as plots of their relative size (on the right). The size of the particles depends on the temperature and on the composition of the supersaturated solid solutions; it is determined by the conditions of formation of crystal nuclei and by the rate of growth of these nuclei.

This type of decomposition reaction in supersaturated solid solutions of metallic systems has been studied in a large number of alloys based on aluminium, iron, nickel, titanium, and other metals. They are of the utmost importance in raising the strength, heat-resistance, and changing other physicochemical properties as a function of conditions, and of the structure of the solid solutions undergoing decomposition and of the phases which are precipitated from them.

We can also suggest general mechanisms for the crystal chemical reactions occurring during eutectoid and peritectoid transformations in metallic systems.

Since a detailed discussion of these reactions is out of the question, we will merely state that eutectoid reactions proceed according to the scheme

$$\text{solid solution } \gamma \rightleftarrows \alpha + AB \text{ (or } \beta \text{ phase)},$$

whereas peritectoid reactions involve the scheme

$$\gamma + \alpha \rightarrow AB \text{ (or } \beta \text{ phase)}.$$

These reactions have their own individual peculiarities, depending also on composition and temperature, and the resulting phases can pass through a succession of intermediate states and exhibit different crystal structures. These reactions are particularly significant when the metals can exist in polymorphic modifications (Fe, Ti, Zr, etc.). These problems are dealt with in general textbooks on solid state chemistry [75] and metallography [18-23].

Surface reactions in alloys, occurring when these materials are heated in air or in special media [75,78-80], are a separate class of crystal chemical reactions. The branch of crystal chemistry concerned with reactions between metals and non-metal powders and with the formation of solid solutions, compounds, and heterogeneous alloy structures [75,81,82] has also attracted a great deal of work.

## 7. INTERACTION BETWEEN INTERMETALLIC COMPOUNDS

The reactions between intermetallic compounds, like reactions between metals, are determined by a number of physicochemical factors, which the writer has previously formulated [83]. The different types of interactions between intermetallic compounds in binary systems of these compounds can be described by means of the three main types of equilibrium diagram (see Fig. 15):

1. System AB–AC (continuous series of solid solutions),
2. System AB–AX (restricted series of solid solutions),
3. System AB–AY (eutectic mixtures without solid solutions).

The following factors are conducive [84] to the formation of continuous solid solutions (Fig. 15*a*) in intermetallic systems: (1) isomorphous crystal lattices of the two compounds; (2) identical chemical bond type; (3) compounds including elements with similar metal chemical properties; (4) compounds of identical stoichiometric composition.

Unless these conditions are met, the intermetallic compounds form only restricted solid solutions (Fig. 15*b*), and in the limit, for very large differences in chemical properties between the components, only mechanical mixtures are

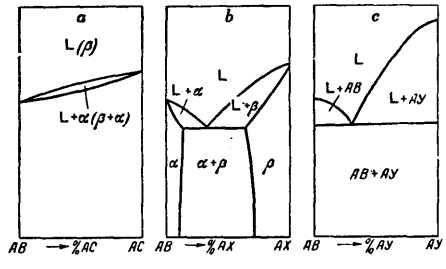



Fig. 15. Types of equilibrium diagram for intermetallic systems:
*a*) continuous solid solutions;
*b*) restricted solid solutions;
*c*) eutectic mixtures without solid solutions.

formed (Fig. 15*c*). All these problems of interactions between intermetallic compounds of different types have attracted a great deal of attention in recent times, and would justify a separate review article.

---o0o---

Thus, our review of the development and present status of the science of metal chemistry leads us to conclude that metal chemistry, as a scientific discipline, can unify the study of the interactions of over 80 metals of the Periodic Table, both with each other and with non-metals. By suitable application of Mendeleev's Periodic Law, metal chemistry establishes the principles which control the formation of the different classes of metallic solutions and compounds.

Metallic solid solutions, as phases of variable composition, have on the whole a single type of chemical bond: the metallic bond. On the other hand, there is a large number of intermetallic compounds showing very different bond types, from metallic to ionic. The study of solid solutions and metal compounds is highly relevant to an understanding of the mode of interaction of many metals, and it makes possible the prediction of equilibrium diagrams for as yet unknown simple and multicomponent metallic systems.


1. M.V.Lomonosov, "Polnoe Sobranie Sochinenii. Tom I. Trudy po Fizike i Khimii" (Complete Collected Works. Vol.1. Papers on Physics and Chemistry), Izd.Akad.Nauk SSSR, 1950.
2. M.V.Lomonosov, "Polnoe Sobranie Sochinenii. Tom V. Trudy po Mineralogii, Metallurgii, i Gornomu Delu" (Complete Collected Works. Vol.5. Papers on Mineralogy, Metallurgy, and Mining), Izd.Akad.Nauk SSSR, 1950.
3. A.I.Sherer, "Rukovodstvo k Prepodavaniyu Khimii" (Chemistry Instruction Manual), Izd.Meditsinskoi Tipografii, St.Petersburg, 1803.
4. B.N.Menshutkin, Izv.Inst.Fiz.Khim.Anal.Akad.Nauk SSSR, 8, 373 (1936).
5. C.J.Karsten, "Handbuch der Eisenhüttenkunde", Vol.I, Berlin, 1841.
6. A.Matthiessen, "Report on the Chemical Nature of Alloys", Report of the 33rd Meeting of the British Association for the Advancement of Science, 1863, p.37.
7. D.I.Mendeleev, "Osnovy Khimii" (Fundamentals of Chemistry), 9th Edn., Vols.I and II, GIZ, 1928.
8. N.S.Kurnakov, "Sobranie Izbrannykh Rabot" (Collection of Selected Works), Vol.II, Khimizdat, 1939, p.5.
9. J.Willard Gibbs, "Thermodynamic Works" (Translated into Russian; edited by V.K.Semenchenko), Gostekhteoretizdat, 1950.
10. G.A.Tammann, "Lehrbuch der Metallographie", Verlag von Leopoldvoss., Leipzig, 1914.
11. W.C.Roberts-Austen, "An Introduction to the Study of Metallurgy", 2nd Edn., London, 1910.
12. H.Le Châtelier, Compt.rend., 130, 85 (1900).
13. H.M.Howe, "Iron, Steel, and Other Alloys", 2nd Edn., Columbia University, 1906.
14. N.S.Kurnakov, "Vvedenie v Fiziko-Khimicheskii Analiz" (Introduction to Physicochemical Analysis), Izd.Akad.Nauk SSSR, 1940.
15. V.Ya.Anosov and S.A.Pogodin, "Osnovnye Nachala Fiziko-Khimicheskogo Analiza" (Fundamentals of Physicochemical Analysis), Izd.Akad.Nauk SSSR, 1947.
16. R.Vogel, "Die Heterogene Gleichgewichte", Leipzig, 1937.
17. F.N.Rhines, "Phase Diagrams in Metallurgy", McGraw-Hill, New York, 1956.
18. A.A.Bochvar, "Metallovedenie" (Metallography), Metallurgizdat, 1956.
19. Ya.S.Umanskii, B.N.Finkel'shtein, M.N.Blanter, S.T.Kishkin, N.S.Fastov, and S.S.Gorelik, "Fizicheskie Osnovy Metallovedeniya" (The Physical Foundations of Metallography), Metallurgizdat, 1955.
20. W.Hume-Rothery, "The Structure of Metals and Alloys" (Translated into Russian), Metallurgizdat, 1945.
21. C.S.Barrett, "Structure of Metals", McGraw-Hill, New York, 1943.
22. F.Seitz, "The Physics of Metals", McGraw-Hill, New York, 1943.
23. L.S.Darken and R.W.Gurry, "Physical Chemistry of Metals", McGraw-Hill, New York, 1953.
24. N.V.Ageev, "Khimiya Metallicheskikh Splavov" (Chemistry of Alloys), Izd.Akad.Nauk SSSR, 1941.
25. N.V.Ageev, "Priroda Khimicheskoi Svyazi v Metallicheskikh Splavakh" (Nature of the Chemical Bond in Alloys), Izd.Akad.Nauk SSSR, 1947.
26. I.I.Kornilov, Uspekhi Khim., 21, 1045 (1952).
27. I.I.Kornilov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 795 (1953).
28. I.I.Kornilov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 397 (1957).
29. "The Physical Chemistry of Metallic Solutions and Intermetallic Compounds", Vols.I and II, National Physical Laboratory Symposium No.9, London, 1959.
30. B.V.Nekrasov, "Kurs Obshchei Khimii" (Course of General Chemistry), Goskhimizdat, 1952, pp.655, 667.
31. L.Pauling, "The Nature of the Chemical Bond" (Translated into Russian), Goskhimizdat, 1947, p.65.
32. H.O.Pritchard and H.A.Skinner, Chem.Rev., 55, 745 (1955).
33. O.K.Rice, "Electronic Structure and Chemical Binding" (Translated into Russian), Inostr.Lit., Moscow, 1949.
34. V.V.Vedeneev, L.V.Gurvich, V.N.Kondrat'ev, V.A.Medvedev, and E.L.Frankevich, "Energiya Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu. Spravochnik" (The Dissociation Energy of Chemical Bonds. Ionisation Potentials and Electron Affinity. Handbook), Izd. Akad.Nauk, 1962.
35. W.Gordy and W.Thomas, J.Chem.Phys., 24, 439 (1956).
36. "Komissiya po Nomenklature Khimicheskikh Soedinenii Akad. Nauk SSSR, Proekt Nomenklatury Neorganicheskikh Soedinenii" (Commission on the Nomenclature of Chemical Compounds, Academy of Sciences of the USSR, Project on the Nomenclature of Inorganic Compounds), Izd.Akad.Nauk SSSR, 1959.
37. W.Finkelburg and W.Humbach, Naturwiss., 42, 535 (1955).
38. J.H.van't Hoff, Z.phys.Chem., 5, 322 (1890).
39. N.S.Kurnakov and S.A.Pogodin, "Iz Istorii Issledovaniya Tverdykh Rastvorov" (History of the Investigation of Solid Solutions), Izv.Sektora Fiz.-Khim.Anal., Inst.Obshch.Neorg. Khim.Akad.Nauk SSSR, 16, 7 (1943).
40. "Trudy Konferentsii po Tverdym Rastvoram" (Proceedings of the Conference on Solid Solutions), Izv.Sektora Fiz.-Khim. Anal., Inst.Obshch.Neorg.Khim.Akad.Nauk SSSR, 16, Nos.1, 2, 3, and 4.
41. N.V.Grum-Grzhimailo, "Khimicheskie Svyazy v Metallicheskikh Splavakh" (Chemical Bonds in Alloys), Izd.Akad. Nauk SSSR, 1960.
42. J.M.Sivertsen and M.E.Nicholson, "The Structure and Properties of Solid Solutions", Pergamon, 1961.
43. N.V.Ageev, "Periodicheskii Zakon Mendeleeva — Osnova Nauki o Metallicheskikh Splavakh" (Mendeleev's Periodic Law: The Foundation of the Science of Alloys), Symposium on the Theory of Alloys, Izd.Akad.Nauk SSSR, 1952.
44. I.I.Kornilov, Dokl.Akad.Nauk SSSR, 73, 495 (1950).

45. M.Hansen and K.Anderko, "Constitution of Binary Alloys", McGraw-Hill, New York, 1958.
46. L.A.Carapella, Metal Progress, 48, 297 (1945).
47. V.G.Kuznetsov, Izv.Sektora Fiz.-Khim.Anal., Inst.Obshch. Neorg.Khim.Akad.Nauk SSSR, 16, 68 (1948).
48. I.I.Kornilov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 475 (1950).
49. I.I.Kornilov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 980 (1953).
50. I.I.Kornilov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 392 (1954).
51. E.M.Savitskii and V.V.Kopetskii, Izv.Akad.Nauk SSSR, Otd. Tekh.Nauk, Seriya Metallurgiya i Toplivo, 157 (1962).
52. I.I.Kornilov and R.S.Polyakova, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 565 (1962).
53. I.I.Kornilov and N.M.Matveeva, Uspekhi Khim., 31, 1076 (1962) [Russ.Chem.Rev., 512 (1962)].
54. I.I.Kornilov, Zhur.Neorg.Khim., 3, 571 (1958).
55. I.I.Kornilov, Dokl.Akad.Nauk SSSR, 128, 722 (1959).
56. N.S.Kurnakov, S.F.Zhemchuzhnyi, and M.I.Zasedatelev, Zhur.Russ.Fiz.-Khim.Obshch., 47, 871 (1915).
57. F.Weibke, Z.Elektrochem., 44, 209, 263 (1938).
58. P.I.Kripyakevich and E.E.Cherkashin, Izv.Sektora Fiz.--Khim.Anal., Inst.Obshch.Neorg.Khim.Akad.Nauk SSSR, 24, 59 (1954).
59. I.I.Kornilov and B.K.Vul'f, Uspekhi Khim., 28, 1087 (1959).
60. G.B.Bokii, B.K.Vul'f, and N.L.Smirnova, Zhur.Strukt. Khim., 2, 74 (1961).
61. G.V.Samsonov, Poroshkovaya Metallurgiya Akad.Nauk Ukrain.SSR, 2 (2), 3 (1962).
62. N.V.Grum-Grzhimailo, I.I.Kornilov, E.N.Pylaeva, and M.A.Volkova, Dokl.Akad.Nauk SSSR, 137, 599 (1961).
63. I.I.Kornilov and V.V.Glazova, Dokl.Akad.Nauk SSSR, 130, 33 (1963).
64. O.Kubaschewski and E.Ll.Evans, "Metallurgical Thermochemistry" (Translated into Russian), Inostr.Lit., Moscow, 1954.
65. Yu.M.Golutvin, "Teploty Obrazovaniya i Tipy Khimicheskoi Svyazi v Neorganicheskikh Kristallakh" (Heats of Formation and Chemical Bond Types in Inorganic Crystals), Izd.Akad. Nauk SSSR, 1962.
66. N.V.Ageev, Zhur.Neorg.Khim., 3, 537 (1958).
67. I.I.Kornilov and N.M.Matveeva, Dokl.Akad.Nauk SSSR, 139, 4 (1961).
68. S.T.Konobeevskii, Izv.Sektora Fiz.-Khim.Anal., Inst. Obshch.Neorg.Khim.Akad.Nauk SSSR, 16, 19 (1943).
69. G.V.Samsonov, L.Ya.Markovskii, A.F.Zhigach, and M.G.Valyashko, "Bor, Ego Soedineniya i Splavy" (Boron, Its Compounds and Alloys), Izd.Akad.Nauk Ukrain.SSR, Kiev, 1960.
70. G.V.Samsonov and Ya.S.Umanskii, "Tverdye Soedineniya Tugoplavkikh Metallov" (Hard Compounds of High-Melting Metals), Metallurgizdat, 1957.
71. G.V.Samsonov, "Silitsidy i Ikh Ispolzovanie v Tekhnike" (Silicides and Their Industrial Applications), Izd.Akad.Nauk Ukrain.SSR, 1959.
72. G.V.Samsonov and L.L.Vereikina, "Fosfidy" (Phosphides), Izd.Akad.Nauk Ukrain.SSR, 1961.
73. G.V.Samsonov and S.V.Rodzinskaya, Uspekhi Khim., 30, 60 (1961) [Russ.Chem.Rev., 28 (1961)].
74. I.I.Kornilov, "Sbornik Dokladov na Soveshchanii po Teorii Metallicheskikh Splavov" (Papers Presented to the Conference on the Theory of Alloys), Izd.Akad.Nauk SSSR, 1952.
75. W.E.Garner, "Chemistry of the Solid State", Butterworth, London, 1955; *ibid.* (Translated into Russian), Inostr.Lit., Moscow, 1961.
76. I.I.Kornilov, Izv.Sektora Fiz.-Khim.Anal., Inst.Obshch. Neorg.Khim.Akad.Nauk SSSR, 20, 294 (1950).
77. A.M.Rubinshtein, Uspekhi Khim., 21, 1287 (1952).
78. V.I.Arkharov, "Okislenie Metallov" (Oxidation of Metals), Metallurgizdat, 1945.
79. O.Kubaschewski and B.E.Hopkins, "The Oxidation of Metals and Alloys" (Translated into Russian), Metallurgizdat, 1961.
80. D.V.Ignatov and R.D.Shamgunova, "O Mekhanizme Okisleniya Splavov na Osnove Nikela" (Mechanism of the Oxidation of Nickel-Base Alloys), Izd.Akad.Nauk SSSR, 1960.
81. M.Yu.Bal'shin, "Poroshkovaya Metallurgiya" (Powder Metallurgy), Mashgiz, 1948.
82. F.Eisenkolb, "Die neuere Entwicklung der Pulver-metallurgie", Verlag Technik, Berlin, 1955.
83. I.I.Kornilov, Dokl.Akad.Nauk SSSR, 81, 597 (1951).

Baikov Institute of Metallurgy

---

U. D. C. 546.26-162

# PYROGRAPHITE (PREPARATION, STRUCTURE, PROPERTIES)

A. S. Fialkov, A. L Baver, N. M. Sidorov, M. L Chaikun, and S. M. Rabinovich

CONTENTS

I. Introduction 46
II. Short description of the methods for the preparation of pyrographite 47
III. Physicochemical processes occurring during the preparation of pyrographite 47
IV. Structure of pyrographite 50
V. Properties of pyrographite 52
1. Density 52
2. Hardness 53
3. Linear thermal expansion 53
4. Mechanical properties 53
5. Thermal conductivity 54
6. Electrophysical properties 54
VI. Uses of pyrographite 56

## I. INTRODUCTION

Pyrolytic graphite is the product of the pyrolysis of hydrocarbons on surfaces heated to 1000–2500°C. In recent years this material has attracted very considerable attention from research scientists, technologists, and engineers working in various fields of science and technology. This is because of the many quite unique properties of pyrolytic graphite. Its strength at temperatures