156. V. N. Ipat'ev, "Kataliticheskie Reaktsii pri Vysokikh Temperaturakh i Davleniyakh" (Catalytic Reactions at High Temperatures and Pressures), Izd. Akad. Nauk SSSR, 1936.
157. K. A. Alekseeva and B. L. Moldavskii, Khimiya Tekhnol. Topliva i Masel, No 1, 43 (1959).
158. C. M. Cawley, Research, 1, 553 (1948).
159. S. Ando, J. Soc. Chem Ind. Japan, 41, 413b (1938); Chem. Abs., 33, 6807 (1939).
160. S. Ando, J. Soc. Chem. Ind. Japan, 43, 328b (1940); Chem. Abs., 35, 1770 (1941).
161. J. Coops, J. W. Dienske, and A. Aten, Rec. Trav. Chim Pays-Bas, 57, 303 (1938).
162. M. Takahashi, Sci. Repts. Tokyo Rayon Co., 12, 128 (1957).
163. S. Fujita, Mem. Coll. Sci., Kyoto Imp. Univ., 23A, 399 (1942); Chem. Abs., 44, 3445 (1950)
164. West German Pat. DBP 857 962 (1952); Chem. Abs., 47, 11239 (1953).
165. U. S. Pat. 2 478 261 (1949); Chem. Abs., 44, 1136 (1950).
166. U. S. Pat. 2 675 390 (1954); Chem. Zentr., 4283 (1956).
167. R. C. Anderson and E. S. Wallis, J. Amer. Chem. Soc., 70, 2931 (1948).
168. R. C. Anderson, Diss. Abs., 15, 334 (1955).
169. I. B. Rapoport, T. Gritsevich, and V. Ilomanov, Khimiya Tverd. Topliva, 7, 545 (1936).
170. L. L. Hirst, H. H. Storch, C. G. Fischer, and Q. C. Sprunk, Ind. Eng. Chem., 32, 1372 (1940).
171. G. Z. Koshel', Thesis, Kharkov, 1955.
172. V. A. Lanin, M. V. Pronina, and M. S. Knyazeva, "Sbornik Khimicheskaya Pererabotka Topliva" (Symposium, Chemical Processing of Fuel), Izd. Akad. Nauk SSSR, 1957, p. 231.
173. I. S. Diner and M. S. Nemtsov, Khimiya Tverd. Topliva, 5, 438 (1934).
174. S. Ando, J. Soc. Chem. Ind. Japan, 42, 171b (1939); Chem. Abs., 33, 8961 (1939).
175. M. Orchin and H. H. Storch, J. Soc. Chem. Ind., 69, 121 (1950).
176. I. V. Kalechits, N. I. Popova, and F. G. Salimgareeva, "Sbornik, Khimicheskaya Pererabotka Topliva" (Symposium, Chemical Processing of Fuel), Izd. Akad. Nauk SSSR, 1957, p. 216.
177. Si. Tszu-vei and I. V. Kalechits, Acta focalia sinica, 2, 152, 333 (1957); Referat. Zhur. Khim., 32763 (1959).
178. A. Hagemann and M. Neuhaus, Brauhkohle, 945, 976 (1931).
179. J. F. Jelinek, Chem. prumysl., No. 1, 4 (1957); Referat. Zhur. Khim., 32763 (1959).
180. C. E. Sensemann, Ind. Eng. Chem., 22, 81 (1930).
181. German Pat., DRP 553 410 (1932); Chem. Zentr., II, 1870 (1932).
182. U. K. Pat. 427 145 (1935). Chem. Abs., 29, 6252 (1935).
183. French Pat. 772 856 (1934); Chem. Abs., 29, 1439 (1935).
184. German Pat. DRP 657 207 (1938); Chem. Abs.. 32, 3774 (1938).
185. V. I. Zabavin, Khimiya Tverd. Topliva, 3, 587 (1932).
186. I. B. Rapoport and M. S. Sudzilovskaya, ibid., 5, 805 (1934).
187. E. O. Ohsol and J. S. Mackey, U. S. Pat. 2 786 873 (1957).
188. M. I. Kuznetsov and K. A. Belov, Khimiya Tverd. Topliva, 4, 592 (1933).
189. M. I. Kuznetsov and K. A. Belov, Ukrain. Khim. Zhur., 12, 412 (1937).
190. V. P. Konov, Khimiya Tverd. Topliva, 7, 711 (1936).
191. I. B. Rapoport and N. P. Masina, ibid., 7, 694 (1936).
192. I. V. Kalechits and F. G. Salimgareeva, Trudy Vost.-Sib. Fil. Akad. Nauk SSSR, No. 3, 79 (1955).
193. I. V. Kalechits and F. G. Salimgareeva, ibid., No. 4, 5 (1956)
194. J. Kosaka, J. Soc. Chem. Ind. Japan, 34, 10 (1931); Chem. Abs., 25, 1971 (1931).
195. B. W. Jones and M. B. Neuworth, Ind. Eng. Chem., 45, 2704 (1953).
196. A. B. Vol'-Epshtein, N. A. Davtyan, M. K. D'yakova, and M. N. Zharova, "Tezisy Dokladov na Soveshchanii po Novym Metodam Ratsional'nogo Ispol'zovaniya Mestnykh Topliv" (Abstracts of Papers given at the Conference on New Methods for the Efficient Exploitation of Local Fuels), Izd. Akad. Nauk Latv. SSR, Riga, 1958, p. 47.
197. K. A. Alekseeva and B. L. Moldavskii, Khimiya Tekhnol. Topliva i Masel, No. 10, 7 (1958).
198. F. Perna and J. Pelčík, Paliva, 33, 126 (1953).
199. U. K. Pat. 519 721 (1940); Chem. Abs., 36, 97 (1942).
200. U. K. Pat. 519 796 (1947); Chem. Abs., 42, 1315 (1948).
201. U. S. Pat. 2 295 672—5 (1942); Chem. Abs., 37, 1132 (1943).
202. U. S. Pat. 2 435 038 (1948); Chem. Abs., 42, 3433 (1948).
203. West German Pat. DBP 874 911; Chem. Zentr., 8206 (1953).
204. East German Pat. 12 422 (1956).
205. N. N. Vorozhtsov Jr. and V. N. Lisitsyn, USSR Pat. 97 056 (1953).
206. N. N. Vorozhtsov Jr. and V. N. Lisitsyn, Zhur. Obshch. Khim., 27, 1770 (1957).
207. J. Pigman, E. D. Bel, and M. B. Neuworth, J. Amer. Chem. Soc., 76, 6169 (1954).
208. P. H. Given, J. Appl. Chem., 7, 172 (1957).
209. D. B. Luten Jr. and G. M. Good, U. S. Pat. 2 514 960 (1950); Chem. Abs., 44, 9479 (1950).
210. P. H. Given, U. K. Pat. 874 911 (1953).
211. G. H. Stillson and J. B. Fischel, U. S. Pat. 2 383 279 (1945); Chem. Abs., 40, 95 (1946).
212. O. H. Dawson, U. S. Pat. 2 366 497 (1945); Chem. Abs., 39, 1881 (1945).
213. J. R. Hoatson and R. H. Rosenwald, U. S. Pat. 2 676 191 (1954); Chem. Abs., 49, 4714 (1955).

Faculty of Chemistry,
Lomonosov Moscow State University

THERMODYNAMICS AND THE STRUCTURE OF METALLIC ALLOYS

A. M. Evseev

CONTENTS

Introduction 320

1. Thermodynamics of liquid alloys with a eutectic in the solid state 321

2. Liquid alloys of systems with compounds in the solid phase 325

3. Ordering processes in solid solutions 326

INTRODUCTION

The atomic or molecular structure of solids is determined by the nature of the forces acting between particles. Crystal chemistry is based on the concept that solids acquire a crystal structure corresponding to the chemical bond

type. The thermodynamic method permits quantitative evaluation of the energy of interatomic bonds, but only if an equilibrium structure obtains and is known.

Practical problems often require predictions of the thermodynamic properties of condensed phases. A knowledge of the connection between the structure-sensitive properties of these phases and simple, known, and easily available data is also desirable. A complete solution of such a problem is obviously impossible unless due account is taken of all three of its facets: the crystal-chemical correspondence between bond type and crystal structure, theoretical analysis of the laws governing the interactions between particles, and verification that theoretical conclusions agree with the experimental results of thermodynamic studies.

In the past insufficient attention has been paid to the connection between the thermodynamic properties of metallic alloys and their structure and bond type. The experimental and theoretical study of the connection between alloy structure and thermodynamics has recently gained fresh impetus from work on heat-resisting alloys and semiconductor compounds, especially as regards the statistical theory of ordering processes and the experimental study of short-range ordering in alloys.

It seems desirable, therefore, to clarify the relationship between the structure and thermodynamics of metallic alloys from both the physicochemical and the physical viewpoints. The problem can be subdivided into a number of more or less independent but intimately interconnected sections.

First of all, the calculation of equilibrium thermodynamic properties of alloys on the basis of atomic properties in the light of solution theory must obviously rest on the statistical method. Attention must therefore be directed to statistical methods that are more or less convenient for calculating the thermodynamic functions of alloys. The most rational statistical methods require either the experimental determination or the theoretical calculation of the alloy (or solution) structure. In this connection the problem arises of establishing the link between the structure and the thermodynamic properties of alloys.

Crystal chemistry gave us a deeper insight into the nature of the chemical bond and the rules of formation of molecules and crystals. We can hope that the quantitative characterisation of the chemical bond by combined thermodynamical and structural data will enable us to systematise and generalise our knowledge of liquid and solid metallic alloys.

1. THERMODYNAMICS OF LIQUID ALLOYS WITH A EUTECTIC IN THE SOLID STATE

The formation of an alloy from the pure metals according to the reaction

$$a\,\mathrm{M} + b\,\mathrm{X} = \mathrm{M}_a\mathrm{X}_b \qquad (1)$$

is accompanied by a change in the free energy of the system

$$\Delta F = -RT\ln K_p, \qquad (2)$$

where K_p is the equilibrium constant, a change in the heat content

$$H_{\mathrm{M}_a\mathrm{X}_b} - (aH_{\mathrm{M}} + bH_{\mathrm{X}}) = \Delta H_T \qquad (3)$$

or

$$\Delta H_T = RT^2\frac{\partial \ln K_p}{\partial T}, \qquad (4)$$

and a change in the entropy

$$\Delta S_T = R\left(T\frac{\partial \ln K_p}{\partial T} - \ln K_p\right). \qquad (5)$$

The heat of formation can be experimentally determined by a direct calorimetric measurement of the heat evolved.

The entropy of formation of the alloy may be derived from heat-capacity data by means of the formula

$$\Delta S_T = \int_0^T \frac{\Delta C_p}{T}dT + S_0, \qquad (6)$$

where $S_0 = -R(N_1\ln N_1 + N_2\ln N_2)$ is the configurational entropy of mixing, which must be taken into account for the case of solid or liquid solutions, but not for compounds of stoichiometric composition.

In general, Eqn.(6) is inaccurate, since it is impossible in principle to separate the "configurational" from the "vibrational" entropy. Consequently both the entropy and the enthalpy of formation of the alloy are best determined indirectly from formulae (4) and (5), making use of the experimentally found value of K_p.

The concept of change in partial free energy is often invoked in the study of the thermodynamical properties of alloys:

$$\Delta\mu = \mu_p - \mu_0$$

where μ_p is the chemical potential of the given constituent in the alloy and μ_0 its chemical potential in the pure state; the change in partial enthalpy is

$$\Delta\overline{H} = T^2\frac{\partial(\Delta\mu/T)}{\partial T} \qquad (7)$$

and the change in partial entropy is

$$\Delta\overline{S} = -\frac{\partial\Delta\mu}{\partial T}. \qquad (8)$$

In experimental work it is usual to measure either the e.m.f. of the cell

$$\mathrm{M}_1\,|\,\mathrm{M}^+_{\mathrm{I(ion)}}\,|\,(\mathrm{M}_1\mathrm{M}_{11})_{\text{alloy}}, \qquad (9)$$

which is related to $\Delta\mu$ by the expression

$$\Delta\mu = -23\,066\,zE, \qquad (10)$$

or the vapour pressure of one of the alloy constituents in the pure state (p_0) and in the solution (p_1), when

$$\Delta\mu = RT\ln p_1/p_0. \qquad (11)$$

The partial thermodynamic functions are then derived from formulae (7) and (8). The integral thermodynamic functions, referring to 1 mole of the alloy, are related to the partial quantities by the expression

$$\Delta G = N_1\Delta\overline{G}_1 + N_2\Delta\overline{G}_2. \qquad (12)$$

Alloy formation thus always results in a decrease in the free energy of the system and in the chemical potential of each of the constituents; enthalpy changes characterise the changes in interatomic-bond energy, and entropy changes describe the degree of randomness with which the atoms are distributed. Both functions are related to the atomic-interaction forces and the atomic structure of the alloy.

The present article is limited to consideration of the relation between short-range order and the thermodynamic properties of alloys. The restriction is justified, on the one hand, by the fact that interatomic forces are short--range forces, and, on the other, by the fact that short--range order is also determined by long-range order. The term "short-range order" usually refers to the number and kind of atomic neighbours surrounding a given atom, in the first, second, and possibly the third coordination shells.

In liquid metals and alloys short-range order is defined by the atomic radial distribution function $\rho(r)$, which gives the distribution of atoms in the space surrounding any given atom whose position is taken as the origin of the coordinate system. The number of atoms in a spherical shell $4\pi r^2 dr$, at a distance r from the central atom, is determined by the radial distribution function:

$$dn = \rho(r)\,4\pi r^2 dr.$$

Corresponding to this definition of the radial distribution function, the coordination number of a liquid is given by

$$z_1 = \int_{r_1}^{r_2} \rho(r)\,4\pi r^2 dr, \qquad (13)$$

where r_1 and r_2 are the radial distances from the given atom to the inner and the outer boundaries of the spherical coordination shell.

The radial distribution function is established experimentally from the diffraction of X-rays or electrons by the liquid[1].

From the results of experimental studies of the structure of liquid alloys, the presence of "microheterogeneity" and "stratification" can be expected, and, indeed, in some cases has been definitely established, within the domain of short-range order.

This phenomenon presents a simple picture: as far as nearest neighbours are concerned, an atom of one kind is surrounded by atoms of that same kind. It is evident that this picture represents a statistically average state, and therefore an equilibrium state, i.e. one corresponding to a minimum free energy.

Attempts are sometimes made to describe the phenomenon by means of the ideas and formulae of fluctuation theory, and the formation of clusters is described as a fluctuation. It is obviously understood that the equilibrium distribution under a given set of conditions is a uniform, random distribution of atoms of both kinds.

The following objections may be raised to such a view. In the first place, our picture was derived from X-ray or electron-diffraction data, which reveal *equilibrium* distributions of atoms. Secondly, the probability of a fluctuation increases with temperature according to the formula

$$W_\Phi = ce^{-A_\Phi/kT}$$

where A_Φ, the fluctuation energy, is an essentially positive quantity, such that A_Φ may substantially decrease with increase in temperature. Consequently, the short-range clustering ("stratification") or molecular heterogeneity should increase with temperature if it originated from fluctuations. Experiments show the opposite to be the case. The radial distribution functions for Al–In alloys at two temperatures[2] are shown in Fig. 1. Molecular heterogeneity can be seen to vanish as the temperature is increased: the separation of the first maximum into three peaks decreases

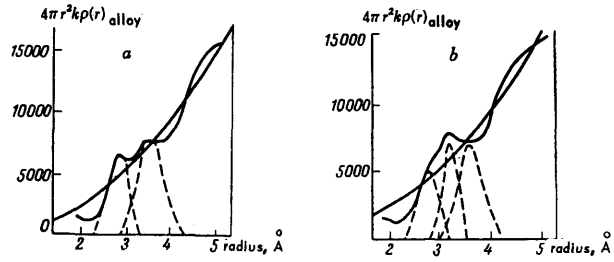


Fig. 1. Radial distribution function for the Al— In alloy: *a*) at 680°; *b*) at 750°.

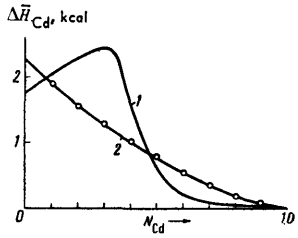


Fig. 2. Partial heat of formation with respect to cadmium in Cd — Pb alloys: 1) at 623°K; 2) at 773°K.

or completely disappears and is replaced by a single maximum which characterises the uniform distribution.

Precisely the same behaviour is observed on studying the thermodynamic properties of systems which form a eutectic in the solid phase. Data for the heat of mixing of liquid alloys of cadmium and lead at two temperatures are reproduced in Fig. 2.

The partial heat of mixing for cadmium at 350°C is a complicated function of composition in no way resembling the curve for regular solutions. At 500° the curve is considerably smoother and has already lost its point of inflection and maximum. Although there are no direct experimental data on the structure of liquid Cd–Pb alloys, we can nevertheless conclude, by analogy with the Al–In alloys, that the smoothing of the $\Delta\bar{H}_{Cd}$ curve results from the disappearance of molecular heterogeneity. Conversely, the complex shape of this curve at low temperatures, near the liquidus temperatures, is definitely connected with the presence of short-range "stratification" or molecular heterogeneity.

Thermodynamic data alone do not establish with complete certainty that molecular heterogeneity of the "stratification" type is present in all liquid alloys that show a more or less extended eutectic field in the solid region of their phase diagram. This is obviously due to the fact that in different systems full miscibility (random distribution of atoms of different kinds) sets in at different temperatures.

For example, the structure of Zn–Sn alloys cannot be unambiguously determined. Practically all liquid alloys of the Zn–Sn system appear to have a completely random distribution of the two kinds of atom. The partial heat of mixing[3] is almost linear. Only in the region of low tin

concentrations is a deviation from linearity observed. The integral heat of mixing gives an asymmetric curve whose maximum is displaced from the 1 : 1 composition to ~0.6 atom fraction of zinc. A similar displacement is also observed with other eutectic systems. The Zn–Sn system can thus be said to exhibit a noticeable, though weak, degree of "stratification".

A completely unambiguous correspondence between the quasi-eutectic structure of the liquid alloys and the thermodynamic properties can be demonstrated with the Pb–Sn system. According to Danilov[4] and Skryshevskii[5] the Pb–Sn alloys show a high degree of inhomogeneity in their short-range order. Thermodynamic studies[6] have shown that the integral heat of mixing of liquid Pb–Sn alloys varies with concentration in the same sense as the heat of formation of solid alloys (Fig. 3). The Pb–Sn phase diagram has two narrow solid-solution fields: lead in tin and tin in lead. Accordingly, the integral-heat-of-formation curve for solid alloys has two branches: one positive, the other negative. The same two branches appear in the heat of mixing curve for liquid alloys. Thus the mode of interaction of lead and tin atoms and the short-range order in their liquid alloys are similar to those in the solid alloys.

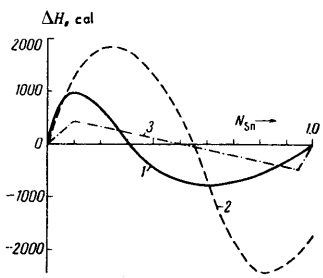


Fig. 3. Heat of formation of Sn — Pb alloys at 1030°K: 1) integral, for liquid alloys; 2) partial, for lead; 3) integral, for solid alloys.

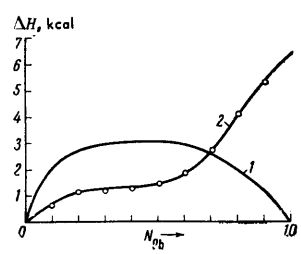


Fig. 4. Heat of formation of Pb — Ag alloys: 1) integral; 2) partial with respect to silver.

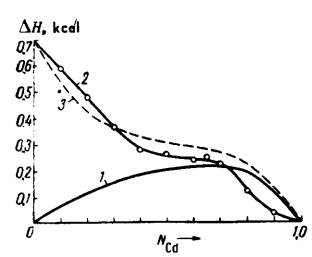


Fig. 5. Heat of formation of Cd — Bi alloys: 1) integral; 2) partial with respect to cadmium; theoretical curve.

The Pb–Sb system exhibits similar thermodynamic properties[7], and its equilibrium phase diagram is analogous to that of the Pb–Sn system. Here, too, we observe two solutions whose heats of formation have opposite signs.

The systems discussed (Pb–Sn and Pb–Sb) form liquid alloys in which the heat of mixing changes sign with change in composition. We shall call them alloys of the first type.

Eutectic alloys have thermodynamic functions of a different type for the liquid state when their phase diagram does not show solid solutions at the two composition extremes.

As mentioned above, the maximum in the integral heat of mixing is displaced towards one of the components and often has the appearance of a sloping plateau. This behaviour is observed especially with Cd–Bi and Ag–Pb alloys. The partial heats of mixing for cadmium and silver in these alloys have a sloping trend in the middle concentration region (Figs. 5 and 4)[8,11,12].

The non-regular concentration dependence of the partial heats of mixing for cadmium and silver can be analytically expressed by an equation, derived by Evseev[11], which involves empirical constants describing the deviations from complete randomness of the distribution of the two kinds of atom.

The partial heat of mixing is given[11] by

$$\Delta\bar{H}_1 = \Delta\bar{H}_\infty \cdot x_2 + \frac{x_1 A x_1 x_2\, e^{-Ax_1x_2/kT} + x_2 B x_1 x_2 e^{-Bx_1x_2/kT}}{x_1 e^{-Ax_1x_2/kT} + x_2 e^{-Bx_1x_2/kT}}, \qquad (14)$$

where $\Delta\bar{H}_\infty$ is the experimentally observed partial heat of mixing, when the first component is infinitely dilute.

The values of the coefficients A and B in Eqn. (14) can be selected on the basis of the activity coefficient at several concentrations. The partial heat of mixing can then be evaluated by substituting these values into the formula.

The calculated and the experimental values of the partial heat of mixing for cadmium in the Cd–Bi system are compared in Fig. 5. The theoretical curve is computed from the equation

$$\Delta\bar{H}_{Cd} = 650\, x_2 + \frac{961 x_1^2 x_2 e^{-0.714x_1x_2} - 1222 x_1 x_2^2 e^{-0.908x_1x_2}}{x_1 e^{-0.714x_1x_2} + x_2 e^{+0.908x_1x_2}}$$

Good agreement is obtained between experiment and theory. It follows that, in general, Eqn. (14) correctly describes the influence of an ordered distribution of atoms on the thermodynamic properties of alloys. However, in some cases the dependence of structure on concentration cannot be limited to the first approximation.

It would be interesting to express the variation of the thermodynamic functions with concentration by substituting into formula (14) experimental data on the structure of the solutions. But one important obstacle arises. In the majority of cases the number of neighbours of the opposite kind, which is needed for calculating the interaction energy in alloys, cannot be evaluated with sufficient precision from diffraction data on the liquid alloys, only general information on the structure of liquid alloys being available.

The absence of a theory of the binding forces in condensed phases (metals, in particular) suitable for practical applications is a further obstacle to the theoretical calculation of the thermodynamic functions of alloys.

At the present time we can only compare thermodynamic

TABLE 1. Coordination numbers for Al—Sn alloys (60% Al).

	n	r_0 Å
Al—Al	10.0	2.70
Al—Sn	1.0	3.05
Sn—Sn	6.2	3.40
Sn—Al	1.5—1.6	3.05

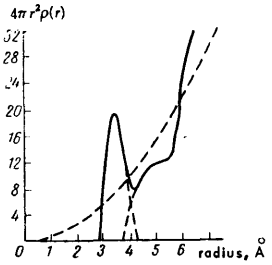


Fig. 6. Radial distribution function for Bi—Pb alloys.

data with an alloy structure on which X-ray and electron-diffraction information already exists. Only a few liquid alloy structures have so far been investigated.

Bublik and Buntar'[12] applied the electron-diffraction method to the study of the structure of liquid Al—Sn alloys. Three maxima, corresponding to the Al—Al, Al—Sn, and Sn—Sn spacings, can be clearly distinguished in the radial-distribution curves for these alloys (see Table 1).

Solid Al—Sn alloys show a wide eutectic region in the phase diagram. In the liquid too, as shown in Table 1, atoms of the same kind are the preferred neighbours, in spite of the fact that a continuous series of liquid solutions is formed. The quantity r_0 in Table 1 is the preferred atom-pair separation in the liquid.

The thermodynamic study of the liquid Al—Sn alloys[13] has not been carried to completion. The work was done at a temperature too high for the effect of molecular heterogeneity on the shape of the heat-of-mixing curve to be pronounced. We can nevertheless observe a shift in the maximum of the ΔH curve, characteristic of eutectic alloys.

Skryshevskii[5] investigated the structure of Bi—Pb alloys of eutectic composition (Fig.6). Danilov and Radchenko[14] had earlier shown qualitatively, from the intensity of scattered X-rays, that atoms of the same kind tend to come together in alloys of eutectic composition. Skryshevskii demonstrated quantitatively that two types of atomic packing exist in eutectic alloys: one with the lead structure and one with the bismuth structure.

The heat of mixing for bismuth-lead alloys[15] does not depart appreciably from regular behaviour, but the partial heat of mixing does, probably owing to the presence of alloys with a quasi-eutectic structure. Partial heats of mixing calculated from formula (14) are in satisfactory agreement with the experimental results. Since formula (14) expresses the functional dependence of the thermodynamic functions on the alloy structure, it follows that we can draw conclusions on the departure of the structure of Bi—Pb alloys from a uniform distribution of atoms of the two kinds by comparing calculated and experimental data.

The Pb—Sn system has been studied by Danilov[16] and, in greater detail, by Skryshevskii[5]. The area under the first maximum of the radial-distribution curve for the eutectic alloy was found to correspond to the sum of the areas for the pure metals. The maximum occurs at r = = 3.26 Å. Consequently, the short-range order in the alloy is similar to that in the pure metals.

However, as already pointed out (Fig.3), the trend of the curve of heat of mixing against concentration for liquid Pb—Sn alloys indicates that structural elements of primary solid solutions are present in the liquid alloys. In other words, not all nearest neighbours are of the same kind as the central atom. It is not possible at the present time to compute the composition of the first coordination shell. This is due to the difficulty of interpreting the experimental data on the structure of liquid alloys and to the low precision with which the area under the maximum of the radial distribution curve can be determined.

Sn—Bi alloys have been studied[17] by electron diffraction. It was found that only with the alloy of eutectic composition could short-range order of the stratification type be demonstrated. All other alloys could be better described by a random distribution of the two kinds of atom.

This is confirmed by the fact that the curve of heat of mixing against concentration has a maximum at the 1 : 1 composition and only a small degree of asymmetry in the direction of bismuth[18]. The system obviously approximates to regularity, both as regards its structure and its thermodynamics, and the small amount of "stratification" at the eutectic composition results from the fact that the structure was studied at a temperature low enough to retain the quasi-eutectic, near the liquidus temperature.

The structure of Zn—Sn alloys was investigated by Lashko[19] at several concentrations, and found to approximate to a completely random distribution of atoms. In no case could the existence of ordering be clearly demonstrated.

The partial heat of mixing for zinc is approximately linear[3] over a wide range of compositions. But the integral-heat-of-mixing curve has a maximum at 0.6, not 0.5 atom fraction of Sn, which denotes non-regularity of the thermodynamic properties of the system.

It should be noted that these departures from the infrequently encountered regular-solution case are not exhibited exclusively by the concentration-dependence of the heat of mixing. Many systems which form eutectics in the solid state have activity coefficients varying with composition in a complicated way. Statistical theory[11] gives the following expression for the activity coefficient in systems comprising two kinds of lattice:

$$\log k_1 = \log\left(x_1 \cdot e^{-(E_{11}-E_{10})/kT} q_{11} + x_2 \cdot e^{-(E_{12}-E_{10})/kT} q_{12}\right). \qquad (15)$$

The variation of the activity coefficient with concentration is therefore determined by the variation of E_{11} and E_{12} with concentration, and therefore also by the structure of the solution or by the short-range order in the atomic distribution (provided that interatomic forces are sufficiently short-range).

Wagner[20] drew attention to the fact that the formulae of the quasi-chemical method do not satisfactorily represent the variation of $\log k_{Cd}$ with concentration in the Cd—Sb system. The same applies to $\log k_{Cd}$ in the Bi—Cd system (Fig.7).

Many eutectic alloys (e.g. Ag—Pb, Pb—Sn, Pb—Sb) have activity coefficients varying with composition in a complicated manner. The concentration-dependence of $\log k$ for

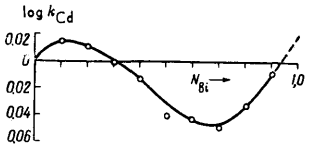


Fig. 7. Concentration dependence of the activity coefficient of cadmium in the Bi — Cd system.

these alloys may be satisfactorily described by assuming the same approximate variation with concentration of E_{11} and E_{12} as in the calculation of the partial heat of mixing.

Consideration of the currently available data on the structure of liquid alloys in conjunction with the thermodynamic properties of these alloys thus leads to the conclusion that the structure in general corresponds with the thermodynamic properties. The statistical theory of solutions, based on a specific model of their molecular structure, can reveal the link between the two approaches. However, there are not sufficient data for a theoretical calculation of the thermodynamic properties of liquid alloys, and furthermore the determination of the structure of liquid alloys still presents grave difficulties.

In conclusion, mention may be made of the so-called positive and negative deviations of the activity from Raoult's law. Negative deviations of the activity from the atom fraction are very often said to denote the presence of intermetallic compounds in the liquid phase or the formation of atomic groupings of the intermetallic compound type. Positive deviations, on the other hand, are ascribed to a tendency of the solution towards stratification. This incorrect opinion is expressed by several authors, who base their views on the early publications of Taylor[21] and Wagner[22].

By comparing the $\log k$ curves for the Cd–Bi and Sn–Pb systems with the data on the structure of these eutectic alloys we find that the activity of the components can exhibit either positive or negative deviations from Raoult's law if the system tends towards stratification. These deviations are induced by an ordered structure of a single type: stratification. It is only possible, therefore, to judge whether the ordering of the structure belongs to the "stratification" or to the "compound formation" type on the evidence of a complete analysis of the thermodynamic data, based on formulae such as (14) and (15).

Conclusions about the structure of a solution should on no account be considered reliable if they are derived merely from the variation of activity with concentration.

2. LIQUID ALLOYS OF SYSTEMS WITH COMPOUNDS IN THE SOLID PHASE

It is desirable to compare the data on the structure of liquid alloys which form one or more compounds in the solid phase with the corresponding thermodynamic parameters. The compounds may be either of the berthollide or of the daltonide type. Starting from the general proposition, put forward by Danilov[4], of corresponding solid- and liquid-alloy structures, we can suggest that order of the "compound-formation" type exists in both liquid and solid alloys, i.e. that as far as short-range order is concerned the structure of the liquid alloys is similar to that of the compound in the solid phase.

In the Au–Sn system the solid-phase compounds AuSn, $AuSn_2$, and $AuSn_4$ can be distinguished. Skryshevskii[5] and Hendus[23] made X-ray studies of the structure of liquid alloys of composition AuSn. It was found that each Sn atom is surrounded by 6.5 atoms of Au, and the Au atom is also surrounded by 6.5 Sn atoms. These experiments were carried out at 450°, i.e. near the liquidus temperature.

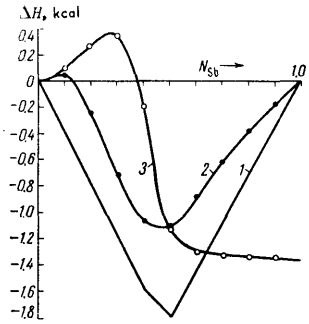


Fig. 8. Heat of formation of Cd — Sb alloys: 1) integral, for solid alloys; 2) integral, for liquid alloys; 3) partial with respect to Cd.

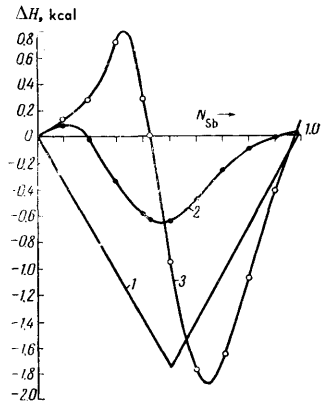


Fig. 9. Heat of formation of Zn — Sb alloys: 1) integral, for solid alloys; 2) integral, for liquid alloys; 3) partial with respect to Zn.

The atomic distribution found for the liquid alloy corresponds to that for the solid alloy of the same composition. Clearly, as in the case of eutectic alloys, the given atomic distribution is only an approximation to the actual state of affairs. A fraction of the Sn atoms may exchange places with Au atoms. Available structural data are insufficient for a precise calculation of the number of nearest neighbours of the two kinds.

The heat of mixing for Au–Sn alloys has been measured[24] at 550°, and does not reveal any departures from regularity. This is hard to explain, especially since a number of alloys of the same type give quite appreciable effects. Kleppa[24] found that the entropic contribution of Sn at 550° shows a peculiar concentration-dependence, which Frost attributes[25] to ordering processes in the liquid phase.

Solid alloys of the Cd–Sb system are characterised by the presence of the compounds CdSb and Cd_3Sb_2. No structural studies of the liquid alloys of this system have been published, but one can nevertheless expect to find short-range order in them by analogy with the Au–Sn system.

By comparing the thermodynamic data[26,27] for the solid and liquid alloys (Fig.8) we can conclude that the solid and liquid structures are of a similar character. The heat of formation of the liquid alloys at the eutectic composition is positive. The subsequent trend of the heat-of-mixing curve is surprisingly reminiscent of the heat-of-formation curve for the solid alloys. It follows that short-range order of the "compound-formation" type exists in the liquid alloys.

In the Zn–Sb system there are three compounds of composition between 0.5 and 0.6 atom fraction of zinc. The heat of formation of the solid alloys at 20°, and the integral heat of mixing for the liquid alloys, are shown in Fig.9. Once again we find that the concentration dependence of the heats of formation of solid and of liquid alloys shows similar trends. The structure of the solid and liquid alloys can therefore be said to be very similar within the limits of short-range order. No structural investigations of liquid Zn–Sb alloys have been reported.

The peculiar variation with concentration of the partial heat of mixing for zinc and cadmium is noteworthy. The sharp inflection of $\Delta\bar{H}_{Cd}$ in the region of the compounds indicates a reorganisation of the structure of one of the "microphases", or, to put it differently, of a cluster-like heterogeneity of molecular dimensions; this is similar to what takes place in the solid.

The behaviour of the heats of formation of liquid and of solid alloys in the Bi–Mg system[29,30] is analogous to those discussed above. The formation of the compound Mg_3Bi_2 in the solid phase can be recognised by a maximum in ΔH at a composition corresponding to a 3 : 2 ratio. The same maximum can be observed, at the same composition, with liquid alloys. The partial heat-of-mixing curve for magnesium shows an inflection, also at the 3 : 2 ratio. One must therefore presume that a structural correspondence between liquid and solid alloys exists in the Mg–Bi system.

The solid compounds Mg_3Bi_2 and Mg_3Sb_2 have the same type of structure. Accordingly, their thermodynamic functions are similar. The integral and the partial heats of formation of the Mg–Sb alloys therefore vary with concentration just like the corresponding quantities for the Mg–Bi system[27,31].

The curves of the thermodynamic functions of the Mg–Sb system retain the same general appearance for the liquid state as for the solid state. Hence we can conclude that the liquid and the solid state structures for the Mg–Sb system are similar.

The Mg–Pb and Mg–Sn systems are no less interesting than the two systems just discussed. They form the solid compounds Mg_2Pb and Mg_2Sn which, like the bismuth and antimony compounds of magnesium, are valence-bond compounds and have an antifluorite-type lattice.

A review of the thermodynamic properties[13,15,28,29] of these compounds once again confirms that similarity in the liquid and solid states is maintained and provides undeniable evidence of the closeness between the structures of the two states. The variation of the activity coefficient with concentration is complex: an inflection at about 0.6 atom fraction of magnesium denotes a transformation of the structure with change in concentration. This yet again underlines the existence of order of the "compound-formation" type in the liquid alloys.

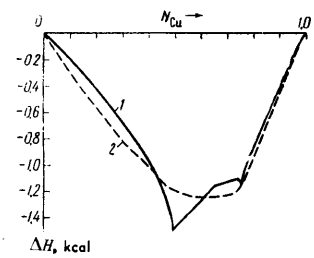


Fig. 10. Integral heat of formation of Cu–Au alloys: 1) below the ordering temperature; 2) above the ordering temperature.

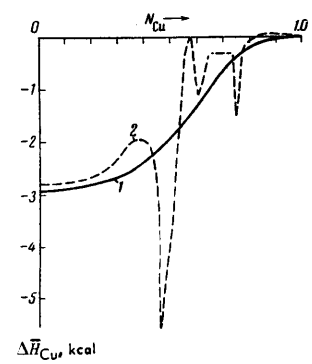


Fig. 11. Partial heat of formation of Cu–Au alloys with respect to Cu: 1) above the ordering temperature; 2) below the ordering temperature.

3. ORDERING PROCESSES IN SOLID SOLUTIONS

Structural studies on various alloys led to the discovery of the phenomenon of ordering in solid solutions. There is no experimental criterion for identifying alloys capable of forming ordered solutions. Not all solid solutions are able to undergo ordering.

Ordering is detected by the appearance in the X-ray diffraction pattern of "superlattice" lines, additional to the lines given by a pure metal with the same lattice. The formation of a superlattice in the Au–Cu alloy having a 1 : 1 ratio of components is a simple example of ordering.

The copper-gold solid solution has a face-centred cubic lattice whose lattice sites can be occupied by any atom with equal probability. When the temperature is lowered it becomes energetically more favourable to let the nearest-neighbour sites surrounding any atom be occupied by atoms of the opposite kind. From the point of view of the quasi-chemical theory of solutions[31] the phenomenon is described by the condition

$$V_{AB} < {}^1/_2(V_{AA} + V_{BB}),$$

where V is the atomic interaction potential. In the cell method the same condition is formulated as follows:

$$E_{11} < E_{12},\ E_{22} < E_{21},$$

where E_{ij} is the energy of the i-th atom in the j-th cell.

As a result, the structure of the solid solution suffers a reorganisation such that each copper atom is surrounded by gold atoms only, and each gold atom by copper atoms only. In the case of AuCu the original solid-solution lattice is not retained: a transformation from the cubic to the face-centred tetragonal form takes place. When the $AuCu_3$ alloy becomes ordered, on the other hand, the lattice of the solid solution

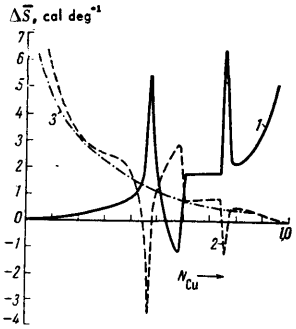


Fig. 12. Partial entropy of formation of Cu–Au alloys: 1) with respect to Au; 2) with respect to Cu; 3) with respect to Cu, above the ordering temperature.

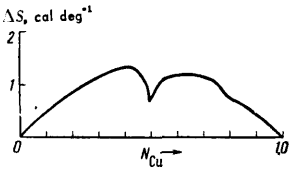


Fig. 13. Integral entropy of formation of Cu–Au alloys below the ordering temperature.

is preserved with only a slight change in dimensions.

It should be mentioned that small heterogeneous fields lie adjacent to the homogeneous fields of the ordered solutions in the phase diagram for the system; the type of the order–disorder phase transition is thus defined.

Bragg and Williams's first statistical theory[32,33] classifies order–disorder changes in alloys among phase transitions of the second kind, which are characterised by a finite jump in heat capacity. But in a transition of the second kind the continuous change in thermodynamic properties with temperature does not admit the existence of heterogeneous regions. Landau[34] showed that the change in lattice symmetry which accompanies phase transitions of the second kind must be taken into account. From the point of view of statistical theory the order–disorder transformation is a mixed phase transition of the first and the second kinds with a continuously changing probability of finding atoms of the two types at their "proper" or at "foreign" lattice sites. Let us now turn to the thermodynamics of copper-gold alloys undergoing ordering.

Oriani[35], and Weibke and Quadt[36], studied the thermodynamic properties of ordered Cu–Au alloys by the e.m.f. method. The heats of formation of Cu–Au alloys at 380° are given in Figs.10 and 11. Alloys of compositions 1 : 1 and 1 : 3, corresponding to CuAu and Cu_3Au, give rise to maxima in the heat-of-formation curve, similar to those accompanying the formation of intermetallic compounds. The main dissimilarity is the absence of an appreciable region, near the ordering composition, over which ΔH varies linearly with concentration.

The variation with concentration of the partial and the integral entropies below the ordering temperature has a characteristic form in the Au–Cu system (Figs.12 and 13). The partial-entropy curves for copper and gold change in the opposite sense in the region of concentrations investigated. The peaks in the partial-entropy curves (Fig.12) obviously define the concentration limits within which ordering can proceed. For ordered solution near $N_{Cu}:N_{Au}$ = = 1 : 1 the curves of $\Delta\bar{S}_{Au}$ and $\Delta\bar{S}_{Cu}$ change smoothly, probably in proportion to the degree of long-range order.

The curve of the change in integral entropy with concentration (Fig. 13) exhibits a minimum at a 1 : 1 ratio, connected with the decreased entropy of formation of this alloy, as required by statistical theory. The "configurational" entropy of formation of the fully ordered alloy is zero. At 380°, near the onset of disorder, both the configurational and dynamic distortions, or fluctuations, of the positions of the atoms become large.

The concentration variation of the thermodynamic properties of the Cu–Au system in its ordered condition depends on the alloy structure. The type of variation can be explained by statistical theory provided that the structure of the alloys is taken into account.

Ordered solid solutions in the Cu–Pt system have also been fairly thoroughly studied from the thermodynamic point of view. Here, too, ordered solutions with compositions CuPt and Cu_3Pt are formed. Johanson and Linde[37] studied the structure of Cu–Pt alloys and found a face-centred cubic lattice for disordered solid solutions. Ordered alloys of composition Cu_3Pt have also the same lattice.

In the region of 40–55 at.% Pt a rhombohedral structure, resulting from the deformation of a cubic lattice, is imposed by the appearance of order. Between 60 and 75 at.% Pt a cubic lattice with an ordered distribution of atoms is formed. The partial and the integral entropies[38] of formation of the alloys are analogous to those of the Cu–Au system in their concentration dependence. The integral heat of formation of the Cu–Pt alloys also shows the two characteristic maxima at the atomic ratios 1 : 1 and 1 : 3 respectively.

We can postulate that short-range order exists above the ordering temperature in the solid solutions of the Cu–Au and Cu–Pt systems which undergo ordering, since the nature of the forces of atomic interaction hardly changes above the ordering temperature. Short-range order in ordered solid solutions implies that in the preferred atomic distribution neighbouring atoms are of different kinds. This ordering phenomenon is formally similar to that which takes place in liquid alloys when eutectics or intermetallic compounds occur in the solid phase.

Roberts[39] and Cowley[40] have studied experimentally the short-range order in Cu–Au alloys above the ordering temperature. Table 2 shows some experimental values of the short-range order parameter α_i for several of the innermost shells surrounding a chosen central atom.

The number of Cu atoms in the i-th coordination shell of an Au atom may be determined as follows. Take the first shell, for instance:

$$\alpha_1 = 1 - \frac{n_{Cu}}{m_i x_{Cu}} = 1 - \frac{n_{Cu}}{12 \times 0.5} = -0.133.$$

The required value, $n_{Cu} = 12 \times 0.5 \times 1.133 = 6.8$, can be easily derived. If perfect short-range order existed in the first shell, n_{Cu} would be 8, and therefore α_1 would be -0.33; at the opposite extreme of complete disorder $n_{Cu} = x_{Cu} \times 12 = 6$, and consequently

$$\alpha_1 = 1 - \frac{6}{12 \times 0.5} = 0.$$

TABLE 2. Data for single-crystal Cu—Au alloys.

Coordination shell i	Coordination number m_i	α_i complete order	α_i 425°
1	12	—0.33	—0.133
2	6	1.00	—0.065
3	24	—0.33	0.020
4	22	1.00	0.066
5	24	—0.33	—0.033
6	8	1.00	0.035

TABLE 3. Short-range order parameters for Cu—Pt alloys.

Coordination shell	Complete order: number of like neighbours	Complete order: number of unlike neighbours	α_{id}	α_{exp} (890°)
1	6	6	0	0.00
2	0	6	—1	—0.20±0.06
3	12	12	0	0.00
4	12	0	1	+0.12±0.05

These experimental data provide a clear picture of short-range order in Cu—Au alloys above the ordering temperature. This type of order changes smoothly with concentration, unlike long-range order below the ordering temperature. Therefore, the thermodynamic functions of solid solutions are also smooth functions of concentration.

The partial and the integral heats of formation of copper-gold solid solutions are displayed in Figs. 10 and 11. The general trend of the variation of the integral heat of formation with concentration corresponds to that for the ordered condition. The partial-heat-of-formation curve for copper (Fig. 11) shows a characteristic inflection at the 1 : 1 composition.

Inferences as to the effect of short-range ordering on the thermodynamic functions of the Cu—Au alloys may also be drawn from the variation of the excess entropy for copper with concentration. A minimum at the 1 : 1 composition, clearly related to short-range order, can be observed in the curve.

Short-range order in Cu—Au alloys also affects the way in which the activity coefficient varies with concentration. $\log k$ for copper as a function of concentration has a trend similar to that of the partial heat of formation of the alloy with respect to copper. If we remember that

$$\log k = \frac{\Delta\bar{H}}{2.3\,RT} - \frac{\Delta\bar{S}_{excess}}{2.3\cdot R},$$

the similarity becomes easy to understand. The heat of formation of the alloy provides the major contribution to the departure of the activity from the concentration.

Short-range order has also been studied[41] in copper—platinum alloys at 890°, i.e. above the ordering temperature. Table 3 gives experimental values for the short-range-order parameter.

As in the case of Cu—Au alloys, short-range order is again observed. It is interesting to note that the partial heat of formation with respect to copper shows a clearly defined plateau over a wide range of concentrations, bearing a slight resemblance to the inflection in the corresponding curve for the Cu—Au alloys. In both the copper-rich and the platinum-rich regions the curve coincides with that for the ordered condition: this can be explained if the primary solutions have a similar character above and below the ordering temperature. In view of the fact that short-range order is experimentally established, the practically constant partial heat of formation in the middle region of the curve must be ascribed to ordering. The dependence of the thermodynamic functions of the alloys on short-range order is thus observed for solid as well as for liquid solutions.

Similar relationships between thermodynamic properties of the solid solutions and structure are again found in the Mg—Cd system. Short-range order has not been experimentally studied in these alloys, and neither have the thermodynamic properties of the ordered solid solutions. For the disordered solutions, however, the thermodynamic properties are known[42]. Their dependence on concentration is analogous to that for the Cu—Au system. Since long-range order is observed in the Cd—Mg system, the similarity in properties between the Cu—Au and the Cd—Mg alloys must be ascribed to the influence of short-range ordering.

Dehlinger[43] studied the structure of the ordered Cd—Mg alloys, $CdMg_3$ and Cd_3Mg. The two series of solid solutions (α and β) in the Mg—Cd system have lattices with hexagonally close packed magnesium and cadmium atoms at all concentrations (axial ratio c/a 1.89 and 1.62 respectively); the lattice dimensions decrease as the concentration of the second component increases. Below 253° superlattices are observed. Alloys of compositions Cd_3Mg and $CdMg_3$ have the cadmium and the magnesium lattice respectively, but with an ordered distribution of atoms. Alloys near the composition CdMg also appear to have the Mg and Cd lattices.

A striking similarity between the alloys of the Cd—Mg and the Au—Cu systems above the ordering temperature is revealed by comparing their heat-of-formation-curves. The partial heat of mixing for Mg shows the same trend with concentration as $\Delta\bar{H}$ for copper in the Cu—Au system (Fig. 11). Consequently, by analogy with the Cu—Au system, we can suggest that short-range order is also present in the Cd—Mg alloys above the critical temperature.

It would be wrong to assume that short-range order exists only in those cases in which long-range order is observed below a critical temperature. The appearance of short-range order in the distribution of atoms is caused by binding forces, and these are so general that the above warning applies to any alloy, whatever the type of interatomic force. Thus, short-range order can be detected experimentally in Ag—Au alloys[44], in which no long-range order has been observed. Data on the number of nearest neighbours in solid Ag—Au alloys, obtained by measurements of diffuse X-ray scattering, are presented in Table 4.

Short-range ordering is also observed in α-brass[45]. The "stratification" type of ordering, which is detected in the solid as well as in the liquid alloys, is more frequently referred to as grouping of like atoms. This phenomenon has

TABLE 4. Short-range order in Ag—Au alloys at 400° (quenched).

Composition	Short-range order parameter α_i	Number of nearest-neighbour Ag atoms around each Au atom
AgAu	$\alpha_1=-0.080$ $\alpha_2=+0.01$	6.48
Ag_3Au	$\alpha_1=-0.05$ $\alpha_2=+0.01$	9.45

been studied experimentally in the solid solutions of the Al—Zn and Al—Ag systems.

Guinier and Walker[46] studied the short-range order in the Al—Ag alloy containing about 6 at.% Ag in the field of the δ-phase. At 500° this field appears as a solid solution. Below 450° segregation of the γ-phase takes place. We can therefore expect ordering in these alloys to be of the "stratification" type, i.e. that regions rich either in silver or in aluminium will appear.

The silver-rich microscopic regions of the alloy proved to have a diameter of 16 Å, the aluminium-rich micro-regions 72 Å. These results apply in particular to the partly annealed alloys, at different stages of segregation of the γ-phase, but we can assume that ordering is preserved at high temperatures even though no precise experimental proof exists. The available thermodynamic data for the δ-phase of the Al—Ag system[47] are too scanty to illustrate the effect of short-range ordering of the stratification or grouping type.

The presence of short-range order in alloys is of more frequent occurrence than its absence. This affects not only the thermodynamic properties of the alloys but also several other physical properties. This is why it is so important to establish the connection between the thermodynamic properties and the atomic structure of alloys; this may lead to the development of a statistical theory of alloys, essential for the prediction of alloy properties.

The phenomenon of ordering, as shown above, can in general be subdivided into two types: "stratification" and "compound formation". This applies equally to the liquid and to the solid solutions. The observed direct link between short-range order in liquid solutions and the structure of the corresponding solids confirms Danilov and Radchenko's hypothesis of congruent structures of liquid and solid alloys.

A combined analysis of the thermodynamic and structural data for liquid alloys can throw light on the correctness of the cellular statistical theory, the basis of which was first laid by Frenkel'[48]. According to this theory, atoms in the liquid spend the greater part of their time in vibrational motion within "cells" made up of other atoms, just like atoms in a solid. The introduction of the concept of two kinds of cells[11] gives greater precision to the cellular model of liquids and links the thermodynamic data with the structural data for the liquid.

Eutectic alloys give quasi-eutectic liquid solutions; alloys forming compounds give liquids in which the atomic packing is not very different from the short-range order found in intermetallic compounds. "True" solutions, in which the atoms of both kinds are distributed completely at random, are rarely encountered, and then only if the temperature is sufficiently high.

Ordering is also observed in solid solutions. The thermodynamic functions of these alloys, like those of the liquids, exhibit a characteristic concentration dependence, reflecting the effect of short-range order in the atomic distribution, since these functions appear to be very sensitive to the pattern of nearest neighbours.

The concept of the short-range order includes the number of atomic neighbours not only in the first coordination shell but also in the second and the third. It has not yet proved possible to carry out a precise evaluation of the contribution of these atoms to the interaction energy, but their influence is nevertheless considerable.

In the present review the discussion of structure has been mainly confined to short-range order in the atomic distribution in alloys, both liquid and solid. This seemed justified in view of the importance of short-range order, which can throw light both on the crystallisation of liquid metals and on stabilising (hardening) processes in solid solutions.

Dispersion hardening of alloys is known to be related to their submicroscopic heterogeneity; the interaction of dislocations with atomic agglomeration can be considered as a factor in the stabilising (hardening) process.

From the point of view of statistical theory short-range order also plays an important part in determining the thermodynamic properties of alloys.

It is evident that no further progress towards a complete elucidation of the link between the structure and the thermodynamics of alloys is possible unless long-range order is taken into consideration. Such a wide view of the problem, however, would go beyond the terms of reference of a single review article. The restricted scope of the present review is therefore not entirely arbitrary.

1. A. I. Kitaigorodskii, "Rentgenostrukturnyi Analiz Melkokristallicheskikh i Amorfnykh Tel" (X-ray Structure Analysis of Cryptocrystalline and Amorphous Materials), GITTL, Moscow — Leningrad, 1952.
2. A. I. Bublik and A. G. Buntar', Kristallografiya, 3, No. 1, 32 (1958).
3. N. W. Taylor, J. Amer. Chem. Soc., 45, 2865 (1923).
4. V. I. Danilov, "Stroenie i Kristallizatsiya Zhidkostei" (Structure of Crystallisation of Liquids), Izd. Akad. Nauk SSSR, 1956.
5. A. F. Skryshevskii, "Voprosy Fiziki Metallov i Metallovedeniya" (Problems in Metal Physics and Metallography), Izd. Akad. Nauk Ukrain. SSR, 1957.
6. G. F. Voronin and A. M. Evseev, Zhur. Fiz. Khim., 33, 2245 (1959).
7. H. Seltz and B. J. DeWitt, J. Amer. Chem. Soc., 61, 2594, 3170 (1939).
8. S. Mellgron, ibid., 74, 5037 (1952).
9. A. V. Nikol'skaya and Ya. I. Gerasimov, Zhur. Fiz. Khim., 28, 713 (1954).
10. A. A. Granovskaya and A. P. Lyubimov, ibid., 27, 1437 (1953).
11. A. M. Evseev, ibid., 33, 112 (1959).
12. A. I. Bublik and A. G. Buntar', Kristallografiya, 2, 255 (1957).
13. M. Kawakami, Sci. Reports Res. Inst. Tohoku Univ., 19, 521 (1930).
14. V. I. Danilov and I. V. Radchenko, Zhur. Eksper. Teor. Fiz., 7, 1158 (1937).
15. C. Wagner and G. Engelhardt, Z. phys. Chem., 159A, 241 (1932).
16. V. I. Danilov, A. I. Zubko, and A. I. Danilova, Zhur. Eksper. Teor. Fiz., 19, 243 (1949).

17. N. V. Alekseev and Ya. I. Gerasimov, Dokl. Akad. Nauk SSSR, 121, 488 (1958).
18. H. Seltz and F. J. Dunkerley, J. Amer. Chem. Soc., 64, 1392 (1942).
19. A. S. Lashko, "Voprosy Fiziki Metallov i Metallovedeniya" (Problems in Metal Physics and Metallography), Izd. Akad. Nauk Ukrain. SSR, 1957.
20. C. Wagner, "The Thermodynamics of Alloys" (Translated into Russian), GNTI, Moscow, 1957.
21. N. W. Taylor, J. Amer. Chem. Soc., 45, 2865 (1923).
22. C. Wagner and G. Engelhardt, Z. phys. Chem., 159A, 241 (1932).
23. H. Hendus, Z. Naturforsch., 20, 505 (1947).
24. O. I. Kleppa, J. Amer. Chem. Soc., 71, 3275 (1949); 72, 3346 (1950).
25. B. R. T. Frost (Editor), "Progress in Metal Physics" (Translated into Russian), Vol. 2, GNTI, Moscow, 1958.
26. O. Kubaschewski and F. Weibke, "Thermochemie der Legierungen", Berlin, 1943.
27. H. Seltz and B. I. De Witt, J. Amer. Chem. Soc., 60, 1305 (1938).
28. O. Kubaschewski and A. Walter, Z. Elektrochem., 45, 630, 732 (1939).
29. W. Seltz and O. Kubaschewski, ibid., 43, 743 (1937).
30. F. A. Vetter and O. Kubaschewski, ibid., 57, 243 (1953).
31. A. G. Samoilovich, "Termodinamika i Statisticheskaya Fizika" (Thermodynamics and Statistical Physics), GITTL, Moscow, 1955.
32. W. L. Bragg and E. I. Williams, Proc. Roy. Soc., 145A, 699 (1934).
33. W. L. Bragg, Uspekhi Fiz. Nauk, 16, 977 (1936).
34. L. D. Landau, Zhur. Eksper. Teor. Fiz., 7, 19, 627 (1937).
35. K. A. Oriani, Acta Metallurgica, 2, 608 (1954).
36. F. Weibke and U. F. Quadt, Z. Elektrochem., 45, 715 (1939).
37. C. H. Johanson and I. O. Linde, Ann. Physik, 78, 439 (1925); 82, 452, 459 (1927).
38. F. Weibke and H. Matthes, Z. Elektrochem., 47, 421 (1941).
39. "Sbornik, Sovremennye Fizicheskie Metody v Metallovedenii" (Symposium, Modern Physical Methods in Metallography), GNTI, Moscow, 1956.
40. I. M. Cowley, J. Appl. Phys., 21, 24 (1950).
41. C. B. Walker, ibid., 23, 118 (1952).
42. F. A. Trumbore, W. E. Wallace, and R. S. Craig, J. Amer. Chem. Soc., 74, 132 (1952).
43. U. Dehlinger, Z. anorg. Chem., 194, 223 (1930).
44. N. Norman and B. E. Warren, J. Appl. Phys., 22, 483 (1951).
45. C. E. Birchenall, Trans. Amer. Inst. Min. Met. Engineers, 171, 167 (1947).
46. C. B. Walker and A. Guinier, Compt. rend., 234, 2379 (1952).
47. I. Chipman and T. P. Florids, Acta Metallurgica, 3, 456 (1955).
48. Ya. I. Frenkel', "Kineticheskaya Teoriya Zhidkosti" (Kinetic Theory of Liquids), Moscow — Leningrad, 1945.

Faculty of Chemistry,
Lomonosov Moscow State University