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Abstract

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ON PHASE DIAGRAMS IN SYSTEMS WITH AN ORDERED PHASE

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The results of the theoretical construction of a phase diagram depend to a significant degree on the form of the expression for the configurational energy of an alloy.

Although in various theories the energy of mixing, i.e., the nonadditive part of the energy, depends in different ways on concentration, degree of order, temperature, and pressure, it can always be reduced to the form

$$E_{\text{mix}} = Uc_A c_B + V\eta^2 + W\sigma. \tag{1}$$

Here η is the degree of long-range order; σ is the degree of short-range order; c_A and c_B are concentrations; U, V, and W may be called, respectively, the parameters of the energy of mixing, the energy of long-range order, and the energy of short-range order.

In the most widespread theories of ordering–those of Bethe (^{1}), Bragg and Williams (^{2}), the quasichemical theory (^{3}), and Kirkwood' s theory generalized to arbitrary concentrations (^{4})–the parameters U, V, and W are determined by one and the same material constant $v = 2v_{AB} - v_{AA} - v_{BB}$ (v_{AA}, v_{BB}, and v_{AB} are the energies of individual pairs of atoms). This is a consequence of the fact that in all these theories the energy is taken in an approximation that accounts only for the interaction of nearest neighbors, with the additional condition that v_{AA}, v_{BB}, and v_{AB} do not depend on either temperature or concentration.

The relationship between the parameters U and V may vary from system to system, even if one takes into account only the direct interaction of atoms but also considers the interaction in coordination spheres more distant than the first (^{5}), and the "elastic" energy caused by the difference in the volumes of the component atoms (^{6}), or by the change with concentration of the distances between atoms (^{7}).

The difference among the parameters U, V, and W, however, is due not only to interaction in distant spheres and to the presence of "elastic" energy. This difference is rooted in the very nature of the energy of an alloy, in which, in addition to the energy of direct central interaction of neighboring atoms (E_1), there is the energy of interaction of ions with the generalized electrons (E_2) and the energy of the latter (E_3). In this case the parameter W is apparently connected mainly with the energy E_1. The parameter V may also be determined by the change in the energy E_3 in connection with the occurrence of long-range order (new Brillouin zones) (^{8}), while the parameter U is determined by all three kinds of energy (^{7}).

Thus, in different systems, depending on the nature of the components (valence, electron concentration, affinity, atomic sizes, etc.), the three parameters may be related to one another in different ways. It is therefore obvious that theories in which the energy is characterized by only one parameter v must have limited applicability.

Thus, these theories lead to the following incorrect consequence: in one and the same system, even at different temperatures and con-

processes will occur that lead to a predominance of unlike neighbors and to a predominance of like neighbors.

Indeed, if $v < 0$, then processes associated with an increase in the number of AB bonds will be energetically favorable; when $v > 0$, processes leading to an increase in the number of AA and BB pairs have the advantage. This conclusion, however, contradicts experimental data. For example, in the Au–Ni system at high temperatures there is a tendency toward an increase in the number of pairs of the AB type (short-range order), whereas at lower temperatures there is a tendency toward an increase in the number of pairs of the AA and BB type (decomposition) (^{9}).

Furthermore, the Bragg and Williams theory (^{2}), when applied to systems with a body-centered crystal lattice, does not lead to two-phase separation even at absolute zero, which contradicts the third law of thermodynamics, since solid solutions at $T = 0$ cannot have entropy equal to zero. The Bragg and Williams theory, improved by taking correlations into account (^{4}), already leads to decomposition at low temperatures. However, this theory corresponds to a single type of phase diagram, in which the critical points of decomposition lie at quite definite concentrations ($C_A = 0.22$ at.% and $C_B = 0.22$ at.%).

It is of interest (without going into the question of why, for a given system, one or another relation among the parameters U, V, and W will obtain) to consider what types of phase diagrams correspond to different combinations of these parameters. The problem posed is analogous to that solved in considering the dependence of the type of phase diagrams on the relation between the mixing energies of two phases (^{10}).

For simplicity we shall not take correlations into account, which is equivalent to assuming $W = 0$. We shall use the expression for the free energy of the Bragg and Williams theory (^{2}); at the same time we shall not spell out the expressions for the parameters U and V, and shall assume them to be independent of one another:

$$\begin{gathered}F = E_A c_A + E_B c_B + U c_A c_B + V\eta^2 + RT\left[(c_A + {}^1/_2\eta)\ln(c_A + {}^1/_2\eta) + \right. \\ + (c_A - {}^1/_2\eta)\ln(c_A - {}^1/_2\eta) + (c_B + {}^1/_2\eta)\ln(c_B + {}^1/_2\eta) + \\ \left. + (c_B - {}^1/_2\eta)\ln(c_B - {}^1/_2\eta)\right]. \qquad (2)\end{gathered}$$

Let us note that the quadratic dependence of the ordering energy on the degree of long-range order η can also be obtained without resorting to the nearest-neighbor approximation (^{11,12}).

Using relation (2), one can obtain the following equation for the dependence of the Kurnakov temperatures on concentration:

$$T \;\; = 8 c_A c_B \frac{V}{R}. \qquad (3)$$

If the critical point of decomposition lies on the line of Kurnakov points, then, according to (^{13}),

$$\frac{\partial^2 F}{\partial c_A'^2} = \frac{\Delta c_p}{T}\left(\frac{\partial T}{\partial c_A'}\right)^2. \qquad (4)$$

Calculating, with the aid of (2) and (4), the quantities entering this relation and taking into account that the jump in heat capacity at the Kurnakov point T is equal to

$$\frac{3}{2}\frac{c_A' c_B'}{c_A'^3 + c_B'^3}$$

(see, for example, (^{14})), we obtain

$$c_A' c_B' = \frac{2 - U/V}{12 - 3U/V}. \qquad (5)$$

Here c_A' and c_B' are the concentrations corresponding to the critical points of decomposition.

With the aid of relation (5) and by considering the free-energy curves at different temperatures, including $T = 0$, one can determine how the type of phase

Fig. 1

Figure 1: Fig. 1

diagram depends on the value $\alpha = U/V$. This dependence is shown schematically in Fig. 1. The dashed lines correspond to Kurnakov point lines, and the solid lines to the boundaries of two-phase regions.

Fig. 1. Schematic dependence of the type of phase diagrams on the value of the ratio $\alpha = U/V$.
a) $\alpha \geqslant 4$; *b)* $2 \leqslant \alpha < 4$; *c)* $0 < \alpha < 2$; *d)* $\alpha = 0$; *e)* $-4 < \alpha < 0$; *f)* $\alpha = -4$; *g)* $\alpha = \alpha_0 - kT,\ \alpha_0 > -4$; *h)* $\alpha = \alpha_0 + kT,\ \alpha_0 < -4$; *i)* $\alpha < -4$.

Why the ordinary Bragg-Williams theory does not lead to two-phase behavior is easy to understand if one takes into account that in this theory $\alpha = 4$, i.e., there is no decomposition (Fig. 1a). As a detailed consideration shows, in a system where $\alpha = -4$, three phases are in equilibrium at all temperatures below the critical decomposition point.

Such a result clearly contradicts the Gibbs phase rule and is due to a number of simplifications adopted by us. Thus, as is done in most works on the theory of solid solutions, we assumed that the parameters U and V are constant in a given system. It is sufficient, however, to suppose that α depends even slightly on temperature or concentration for the contradiction with the phase rule to disappear.

Let us assume, for example, that $\alpha = \alpha_0 + kT$; then only one temperature corresponds to the condition $\alpha = -4$, which corresponds to three-phase equilibrium. If $\alpha_0 > -4,\ k < 0$, the phase diagram will have the form shown in Fig. 1g. The diagram in Fig. 1h corresponds to $\alpha_0 < -4,\ k > 0$.

Since the dependence of U and V on temperature and concentration is apparently usually weak, taking it into account should not substantially affect the form of the phase diagram for different α not equal to -4.

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