Fig. 7.5 Activity of component A in a regular solution as a function of the interaction parameter Ω. From O. J. Kleppa, in *Liquid Metals and Solidification*, ASM, Cleveland, 1958.

approximation. According to Henry's law, $\ln \gamma_i^{\circ} = $ constant when component i is dilute, whereas from equation 7.12 we see that $\ln \gamma_i$ approaches a constant value, Ω/RT, asymptotically as $X_i \to 0$. Furthermore the validity of Raoult's law being applicable for the solvent in a solution where Henry's law is obeyed for the solute is also an approximation, since $\ln \gamma_i$ approaches zero asymptotically as X_i approaches unity, from equation 7.12.

7.3 NONREGULAR SOLUTIONS

For systems in which there is considerable deviation from randomness, the expressions derived in the last section are not applicable. For these solutions Guggenheim[1] has derived a relation for $P_{(AB)}$, namely,

$$P_{(AB)} = X_A X_B Z N_0 \left\{ 1 - X_A X_B \left[\exp \left(\frac{2\Omega}{ZRT} \right) - 1 \right] \right\} \quad (7.14)$$

Expanding the exponential in equation 7.14 and eliminating terms of higher order than the second, it is found that

$$\Delta H_m \cong X_A X_B \Omega \left(1 - \frac{2 X_A X_B \Omega}{ZRT} \right) \quad (7.15)$$

$$\Delta S_m^{xs} \cong - \frac{X_A^2 X_B^2 \Omega^2}{ZRT^2} \quad (7.16)$$

$$\Delta G_m^{xs} \cong X_A X_B \Omega \left(1 - \frac{X_A X_B \Omega}{ZRT} \right) \quad (7.17)$$

[1] E. A. Guggenheim, *Mixtures*, Oxford Press, London, 1952.

In the case where $\Omega = 0$, $P_{(AB)}$ in equation 7.14 becomes equal to that in 7.8. When Ω is negative in sign (equivalent to attraction between unlike neighbors), $P_{(AB)}$ calculated from 7.14 becomes greater than the random value expressed by 7.8. For positive values of Ω, the reverse is true. Thus equation 7.14 represents an attempt to express the conditions for more realistic situations. In these cases when $P_{(AB)} \neq P_{(AB)}$ (random), *short-range order* is said to occur. In order to examine this phenomenon further consider a B ion surrounded by Z nearest neighbors. For a random solution the probability that a given ion in this shell is an A ion is simply X_A. For a nonrandom solution the probability p_1 will be different from X_A. The short-range order parameter α_1 is defined as

$$\alpha_1 \equiv 1 - \frac{p_1}{X_A} \quad (7.18)$$

which is equal to

$$\alpha_1 = 1 - \frac{P_{(AB)}}{ZN_0 X_A X_B} \quad (7.19)$$

In principle, one may go out into the second shell and calculate p_2 and α_2, etc., since they will also tend to be different from random.

For complete randomness $\alpha_1 = 0$; for short-range order in which there is a preference for A–B pairs, $\alpha_1 < 0$; and for *clustering* $\alpha_1 > 0$. The reader should be aware that other definitions of the short-range order parameter are in use, so care must be taken when evaluating results. The quantities α_1, α_2, etc., may be measured in many cases by x-ray and neutron diffraction techniques. Some results are shown in Fig. 7.6. This value may be used in turn to calculate Ω from equation 7.14 and ΔH_m may be calculated from equation 7.15. If experimental thermodynamic data exist for ΔH_m, a check on the validity of equation 7.14 may be obtained. Such an examination has been made for several systems. For systems that do not involve transition
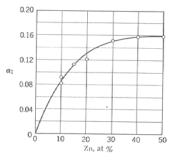

Fig. 7.6 Short-range order in the Al–Zn system as a function of composition at 673°K. From P. S. Rudman and B. L. Averbach, *Acta Met.*, 2, 576 (1954).
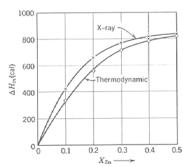
Fig. 7.7 Comparison between heat of mixing in the Al–Zn system calculated from x-ray measurements and direct thermodynamic methods. From P. S. Rudman and B. L. Averbach, *Acta Met.*, 2, 576 (1954).

elements there is often reasonable agreement with the predictions based on the quasichemical theory discussed here and experimental structural data. The solid Al–Zr system is one for which rather good agreement is obtained, as shown in Fig. 7.7. It should be observed that if ΔH_m is positive, Ω is positive. $\alpha_1 > 0$ so that clustering occurs in this system.

By use of an approach similar to Guggenheim the following relations have been derived for the activity coefficients.[1]

$$\gamma_A = \left[\frac{y - 1 + 2X_A}{X_A(y + 1)} \right]^{1/2} \tag{7.20}$$

$$\gamma_B = \frac{y + 1 - 2X_A}{(1 - X_A)(y + 1)}$$

where

$$y = [1 + 4X_A(1 - X_A)(N^2 - 1)]^{1/2}$$

and

$$N = \exp\left(\frac{\Omega}{ZRT}\right)$$

From experimental data for γ, Ω may be determined directly and P_{AB}, for example, may be calculated. In Fig. 7.8 are shown experimental activity data for the liquid In–Sb system which have been fit to a particular value of Ω.

The interaction parameter Ω has been examined in some detail by Averbach.[2] The value of Ω is, in a general case, dependent upon both

[1] G. B. Stringfellow and P. E. Greene, *J. Phys. Chem. Sol.*, 30, 1779 (1969).

[2] B. L. Averbach, in *Energetics in Metallurgical Phenomena*, Vol. II, W. M. Mueller, Ed., Gordon and Breach, New York, 1965.
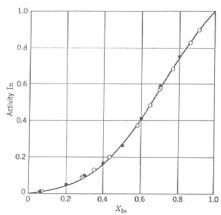
Fig. 7.8 Experimental data for activity of In in the In–Sb system fit to equation 7.19. Ω calculated to be −3980 cal/mol. G. B. Stringfellow and P. E. Greene, *J. Phys. Chem. Sol.*, 30, 1779 (1969).

composition and temperature; let it be assumed that these may be separated. Thus for Ω we may write

$$\frac{\Omega}{ZN_0} = u + j(X) + g(T)$$

For the free energy of mixing, by employing 7.14 and 7.15 we may write

$$\Delta G_m = P_{AB}[u + j(X) + g(T)] - T\,\Delta S_m{}^c$$

where $\Delta S_m{}^c$ is the configurational entropy. Other entropy contributions are obtained from differentiation of the first term on the right-hand side with respect to temperature since $S = -(\partial G/\partial T)_p$. Now

$$\Delta S_m{}^c = k \ln \mathscr{W}$$

and the number of ways of arranging A–A, A–B, B–A, and B–B pairs is

$$\mathscr{W}' = \frac{P!}{P_{AA}!\,P_{BB}!\,P_{AB}!\,P_{BA}!}$$

This term actually contains many unallowable configurations. To illustrate consider a B atom. All pairs involving this atom must be either B–B or B–A pairs. No A–B or A–A pairs are allowed. The expression for W′ is modified,

therefore, to take into account the fact that when $P_{(AB)}$ is that for a random solution, ΔS_m must also equal that for a random solution. The final equation employed is

$$\mathscr{W} = \frac{P!}{P_{AA}!\,P_{BB}!\,P_{AB}!\,P_{BA}!} \left(\frac{N_A!\,N_B!}{N}\right)^Z \left(\frac{N}{N_A!\,N_B!}\right)$$

Upon substitution we find that

$$P_{(AB)} = ZNX_A X_B (1 - \alpha)$$

and recalling that $\Delta S_m = -(\partial\,\Delta G_m/\partial T)_p$ one may derive that

$$\Delta S_m = \Delta S_m{}^c - \frac{\partial}{\partial T}\left[ZN_0 X_A X_B (1 - \alpha)g(T)\right]$$

Solving for $\Delta S_m{}^c$ and recalling that

$$\Delta S_m{}^{xs} = \Delta S_m - \Delta S_m(\text{ideal})$$

we obtain

$$\Delta S_m{}^{xs} \cong |\alpha|\, kN_0[X_A \ln X_A + X_B \ln X_B] - \left\{\frac{\partial}{\partial T}\left[ZN_0 X_A X_B (1 - \alpha)g(T)\right]\right\}$$

and also

$$\Delta H_m = \Delta H_m{}^{xs} = ZN_0 X_A X_B (1 - \alpha)[u + j(X)]$$

For small derivations from ideality

$$\alpha \cong \frac{2X_A X_B[u + j(X) + g(T)]}{kT}$$

Upon examination of the above equation for $\Delta S_m{}^{xs}$, one sees that the sign cannot easily be predicted. The first term on the right-hand side is always slightly negative but the temperature dependence of $g(T)$ may be very large in principle and may be either positive or negative in sign. Also one sees that Ω may not be obtained from thermodynamic measurement of ΔH_m since only the terms $[u + j(X)]$ are involved in the expression for ΔH_m, whereas $\Omega/ZN_0 = [u + j(X) + g(T)]$.

As a simple case, assume that g is linearly dependent upon temperature $[g(T) = gT]$ and let us examine some alloys. From thermodynamic data ΔH_m and $\Delta S_m{}^{xs}$ are often available. The terms $[u + j(X)]g$ and g may be obtained as a first approximation from ΔH_m and ΔS^{xs}, respectively, by assuming that $\alpha = 0$. α is then calculated from the sum $[u + j(X)] + gT$ and substituted back into the expressions for ΔH_m and ΔS^{xs} in order to calculate $[u + j(X)]$ and g again. This process is repeated until consistency is attained. The comparison of thermodynamic calculation with x-ray results is shown in Table 7.1 for several solid alloy systems.

Table 7.1   Short-Range Order Calculations[a]

System (A — B)	Mole frac. B	ΔH_m (kJ/mol)	ΔS^{xs} (J/mol·K)	$N_0[u + j(X)]$ (kJ/mol)	$N_0 g$ (J/mol·K)	Ω/ZRT	α (Thermo)	α (x-ray)
Al-Zn(650°K)	0.2	2.2	0.54	1.2	−0.50	0.17	0.06	0.13
Al-Zn(650°K)	0.5	3.3	0.63	1.2	−0.46	0.17	0.09	0.16
Al-Ag(820°K)	0.10	+0.84	0.42	+0.77	−0.38	0.07	0.01	0.15
Al-Ag(820°K)	0.815	−1.05	4.2	−0.52	−2.3	−0.36	−0.11	−0.09
Cu-Au(720°K)	0.50	−5.1	−0.08	−1.48	−0.23	−0.27	−0.14	−0.13
Cu-Au(720°K)	0.75	−4.4	0	−1.76	−0.29	−0.33	−0.12	−0.15
Au-Ni(1125°K)	0.5	7.3	2.9	2.5	−1.1	0.13	+0.06	0 ±0.05
Au-Ag(800°K)	0.5	−4.6	−1.4	−1.4	0.25	−0.18	−0.09	−0.08

It should again be emphasized that the use of pair potentials is only a convenient way to represent in a statistical sense the gross thermodynamic properties of an alloy. The use does not imply that there are actually covalent bonds between pairs since the terms u and $j(X)$ for a metal include energy contributions from electronic interactions near the Fermi surface which belong to the crystal as a whole as well as ion–ion contribution.

7.4   ORDER–DISORDER TRANSITIONS IN SOLIDS

Atomic Order

Various types of order–disorder reactions may occur in crystals. There is a second-order magnetic transition, for example, in some solids in which a ferromagnetic or antiferromagnetic substance become paramagnetic as the temperature is raised above the critical point. As discussed earlier there exists a change from a superconducting state to nonsuperconducting state for a large number of materials. These processes result from the alignment of magnetic moments in the case of ferromagnetic materials and electron spins in the case of superconductivity In addition to these kinds of processes, long-range atomic ordering processes occur in several alloys. At high temperatures in these systems, the crystal exhibits only short-range order, whereas at low temperatures, the atoms may order themselves in a long-range manner.

Consider as an example an alloy of composition 50 at % A and 50 at % B, which tends to form an ordered phase. That is, the A atoms tend to order themselves on one type of site, α, and B atoms tend to order themselves on another type of site, β, as shown in Fig. 7.9 for a body-centered cubic structure. Let us denote by r_α the fraction of α sites occupied by the right atoms (A atoms) and by r_β the fraction of β sites occupied by the right atoms (B atoms) in an ordered system. The fraction of α sites occupied by

Fig. 7.9 Long-range order on a b.c.c. lattice.

wrong atoms (B atoms), w_α, will be given by

$$w_\alpha = 1 - r_\alpha$$

and the fraction of β sites occupied by wrong atoms (A atoms), w_β, is given by

$$w_\beta = 1 - r_\beta$$

For complete order, $r_\alpha = r_\beta = 1$, and for complete randomness, the probability that an A site is occupied by an A atom is X_A; hence the fraction of α sites occupied by A atoms for complete disorder is X_A. It is convenient to define a long-range order parameter $\mathcal{S}$ in terms of disorder on the α sites as

$$\mathcal{S} \equiv \frac{r_\alpha - X_A}{1 - X_A} \tag{7.21}$$

or, considering disorder on the β sites,

$$\mathcal{S} = \frac{r_\beta - X_B}{1 - X_B} \tag{7.22}$$

From equations 7.21 and 7.22 we see that, for complete disorder, $\mathcal{S} = 0$ and, for complete order, $\mathcal{S} = 1$. For a state of order given by $0 \leq \mathcal{S} \leq 1$, the fraction of A atoms on α sites is r_α. Considering N total sites, there are $(N/2)$ α sites and $(N/2)$ β sites. Thus the total number of A atoms on α sites is $r_\alpha(N/2)$. Substituting in equation 7.21 for $X_A = X_B = \frac{1}{2}$ yields

$$\text{No. of A atoms on } \alpha \text{ sites} = \left(\frac{1 + \mathcal{S}}{4}\right)N$$

$$\text{No. of B atoms on } \beta \text{ sites} = \left(\frac{1 + \mathcal{S}}{4}\right)N$$

The fraction of B atoms on α sites is $(1 - r_\alpha)$ and the number of B atoms on α sites is $(1 - r_\alpha)N/2$. Upon substitution in equation 7.21, we find

$$\text{No. of A atoms on } \beta \text{ sites} = \left(\frac{1 - \mathcal{S}}{4}\right)N$$

$$\text{No. of B atoms on } \alpha \text{ sites} = \left(\frac{1 - \mathcal{S}}{4}\right)N$$

In the body-centered cubic crystal, β sites will be nearest neighbors to α sites. Let us now evaluate the number of A–A pairs, B–B pairs, and A–B pairs for an ordered structure with long-range order parameter $\mathcal{S}$.

The probability that an A atom will be on an α site is r_α, and the probability that an A atom will be on a β site is $w_\beta = (1 - r_\beta)$. Each α site is surrounded by Z β sites, but each pair is counted twice, so the probability of an A–A pair is

$$Z r_\alpha (1 - r_\beta) = \frac{Z(1 + \mathcal{S})(1 - \mathcal{S})}{4} = \frac{Z(1 - \mathcal{S}^2)}{4}$$

The total number of pairs P_{AA} is the probability of an A–A pair times the number of A atoms or

$$P_{AA} = \frac{Z(1 - \mathcal{S}^2)}{4} \cdot \frac{N}{2} = (1 - \mathcal{S}^2)N$$

since $Z = 8$. Similarly the total number of B–B pairs is found to be

$$P_{BB} = (1 - \mathcal{S}^2)N$$

For a solution containing 50 at % A and 50 at % B, the number of A–B pairs is

$$P_{(AB)} = 2(1 + \mathcal{S}^2)N$$

The enthalpy for a gram-atom of solution is

$$H = N_0(1 - \mathcal{S}^2)(H_{AA} + H_{BB}) + 2N_0(1 + \mathcal{S}^2)H_{AB}$$

The configuration entropy is given by

$$S_{cont} = k \ln \mathcal{W}$$

where

$$\mathcal{W} = \frac{(N/2)!}{(\text{No. A atoms on } \alpha \text{ sites})! \, (\text{No. B atoms on } \alpha \text{ sites})!}$$

$$\times \frac{(N/2)!}{(\text{No. A atoms on } \beta \text{ sites})! \times (\text{No. B atoms on } \beta \text{ sites})!}$$

or

$$\mathcal{W} = \frac{(N/2)!}{\{[(1 + \mathcal{S})/4]N\}!\,\{[(1 - \mathcal{S})/4]N\}!}$$
$$\times \frac{(N/2)!}{\{[(1 - \mathcal{S})/4]N\}!\,\{[(1 + \mathcal{S})/4]N\}!}$$

Upon application of Stirling's approximation

$$S_{\text{cont}} = R\{\ln 2 - \tfrac{1}{2}[(1 + \mathcal{S})\ln(1 + \mathcal{S}) + (1 - \mathcal{S})\ln(1 - \mathcal{S})]\} \quad (7.23)$$

In the limit of $\mathcal{S} = 0$, $S_{\text{cont}} = R\ln 2$, which is the entropy for a random solution for $X_A = X_B = \frac{1}{2}$. In the limit of $\mathcal{S} = 1$, $S_{\text{cont}} = 0$ in agreement with what is expected for complete order.

The free energy of solution is

$$G = H - TS$$

and upon substitution

$$G = N_0(1 - \mathcal{S}^2)(h_{AA} + h_{BB}) + 2N_0(1 + \mathcal{S}^2)h_{AB}$$
$$- RT\{\ln 2 - \tfrac{1}{2}[(1 + \mathcal{S})\ln(1 + \mathcal{S}) + (1 - \mathcal{S})\ln(1 - \mathcal{S})]\} - N_0 T s^{\circ}$$
$$(7.24)$$

where s° represents the excess entropy per atom (exclusive of configurational contributions). The entropy, of course, is a maximum when $\mathcal{S} = 0$, or when there is complete randomness. If $\frac{1}{2}(h_{AA} + h_{BB}) > h_{AB}$, the enthalpy term will be reduced and an optimum value of $\mathcal{S}$ will be attained in order to make G a minimum.
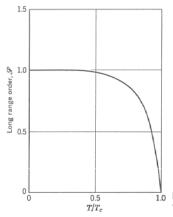
As T increases, S_{cont} becomes more important relative to the enthalpy term, and hence $\mathcal{S}$ diminishes. At a critical temperature, T_c, $\mathcal{S}$ in fact becomes zero. From equation 7.24, the equilibrium value of $\mathcal{S}$ may be calculated as a function of temperature. This is shown below in Fig. 7.10.

The critical temperature T_c is governed by the relation between h_{AB} and $\frac{1}{2}(h_{AA} + h_{BB})$. The lower the energy of the A–B pair in relation to the average of the A–A and B–B mean potentials, the higher T_c will be.

Solution of equation 7.24 yields

$$T_c = -\frac{2[2h_{AB} - (h_{AA} + h_{BB})]}{k} \quad (7.25)$$

Fig. 7.10 Long-range order parameter versus temperature for an AB solution.

and at any temperature different from T_c,

$$\ln\frac{(1 + \mathcal{S})}{(1 - \mathcal{S})} = \frac{2\mathcal{S}T_c}{T} \quad (7.26)$$

This derivation is known as the Bragg-Williams or zeroth-order approximation. At low temperature $\mathcal{S}$ is very close to 1, and as T increases toward T_c, $\mathcal{S}$ decreases very rapidly. This behavior is typical of a cooperative phenomenon. When order is perfect, it is difficult energetically to create disorder (to exchange A and B atoms). As disorder proceeds, however, the process becomes progressively easier from an energetic point of view and finally, in the case of complete disorder, the energy becomes zero for the exchange process. The disordering energy thus depends upon $\mathcal{S}$.

As Fig. 7.10 indicates, according to this calculation the long-range order parameter changes over a range of temperatures. As a consequence the transformation is not first order in nature. The heat capacity, C_p, may be calculated by taking the temperature derivative of the enthalpy. Upon performing this operation, a discontinuity in C_p is found as expected for a second-order transition. The comparison between calculated and measured values of $\mathcal{S}$ as a function of T is shown in Fig. 7.11 for an alloy of 50% Cu, 50% Zn, and a comparison between calculated and experimental heat capacities is shown in Fig. 7.12.

Order–disorder transformations may occur in many different crystal systems. For example, there are transformations in the f.c.c. system such as in Cu–Au alloys at about 25 at % Au, 50 at % Au, and 75 at % Au. These
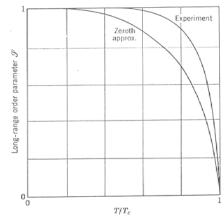
Fig. 7.11 Long-range order parameter as a function of temperature for 50% Cu, 50% Zn. Comparison between theory and experiment.
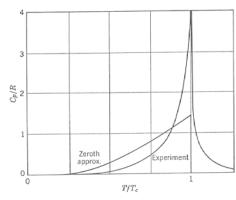

Fig. 7.12 Comparison between experimental and calculated values of C_p for 50% Cu, 50% Zn. Experimental data from F. C. Nix and W. Schockley, *Rev. Mod. Phys.*, **10**, 1 (1938).
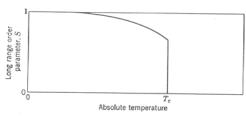
Fig. 7.13 Long-range order parameter $\mathscr{S}$ for an A_3B alloy. From F. C. Nix and W. Schockley, *Rev. Mod. Phys.*, **10**, 1 (1938).

transformations appear to be first order in nature and exhibit $\mathscr{S}$–T curves of the type shown in Fig. 7.13. The Bragg-Williams theory is inadequate in treating these for transformations since it predicts them to be second-order rather than first order in character.

One may readily show that order–disorder transformations do not have to occur at precise chemical compositions but may occur over a composition interval. The further the actual composition is away from the ideal, however, the lower will be the maximum value of $\mathscr{S}$ and T_c. For example, $\mathscr{S}$ obviously cannot have a value of unity if the composition of the alloy is different from 25% A, 75% B, say, since there are three face-centered sites for every one corner site in the f.c.c. structure. In a 20% A, 80% B alloy, for example, some B atoms must by necessity reside on A sites. An example is shown in Fig. 7.14. Note that the maximum value of $\mathscr{S}$ is about 0.8 and T_c is about 640°K. This transition temperature is 20°K lower than that for an alloy which contains 25 at % Au.

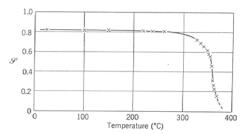Fig. 7.14 Long-range order parameter as a function of temperature for an alloy containing 80 at% Cu and 20% Au. From F. E. Jaumot and C. H. Sutcliffe, *Acta Met.*, **2**, 63 (1954).