

Thermodynamic Properties of Alloy Systems—A Model Approach

7.1 INTRODUCTION

Very few liquid or solid binary systems behave in an ideal fashion. One generally observes that the heat of mixing $\Delta H_m \neq 0$ and often the entropy of mixing $\Delta S \neq 0$. In addition, the curve of ΔH_m versus mole fraction is often not symmetric about the value $X_A = X_B = 0.5$. Some thermodynamic results for alloy systems are shown in Figs. 7.1, 7.2, and 7.3, which illustrate

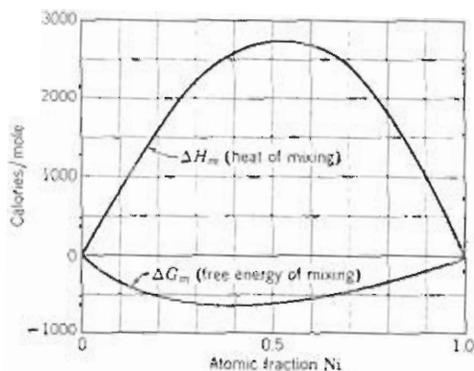


Fig. 7.1 Experimental values of the heat of mixing and free energy of mixing in the Au-Ni system. From B. L. Averbach et al., *Acta Met.*, 2, 92 (1954).

a variety of behavior. From a fundamental point of view, the thermodynamic behavior of alloy systems is very difficult to calculate in practice although the general principles may be rather well understood. In forming an alloy from the pure elements one mixes ions of the solute element with ions of

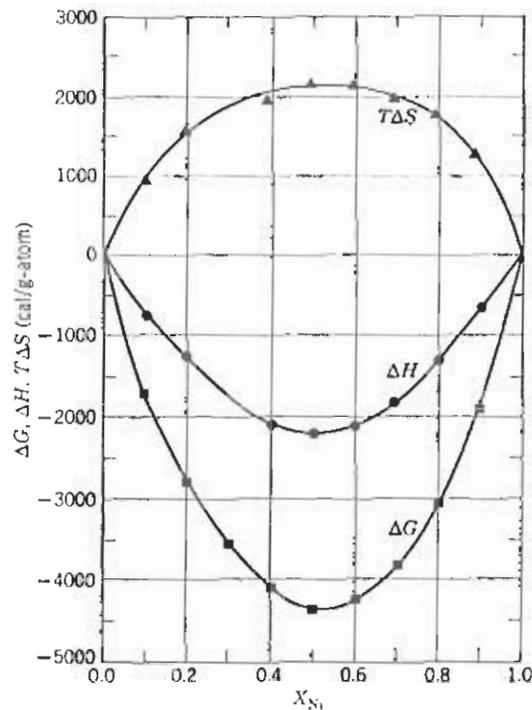


Fig. 7.2 Free energy of mixing, heat of mixing, and entropy of mixing in the Ni-Pt system at 1625°K. Broken curve represents ideal entropy of formation. From R. A. Walker and J. B. Darby, *Acta Met.*, **18**, 1261 (1970).

solvent. In calculating thermodynamic quantities one should consider the repulsion between ion cores, the interaction between cores and electrons at the Fermi surface, as well as other effects. Significant steps are being made in calculation of thermodynamic properties from first principles for some simple alloy systems but as yet no general, easy to apply procedure is available. As a consequence, one devises various types of models which are useful in providing some understanding of alloy behavior as well as in correlating this behavior with other properties. A useful model approach is to assume that one may treat the interaction between ions in a solute by a pairwise model. That is, the properties of a system may be represented by the sum of interactions between neighboring pairs of ions and any complications due to three-body interactions, for example, may be ignored. Some justification for the validity of this approach is obtained from application of pseudo-potential theory.

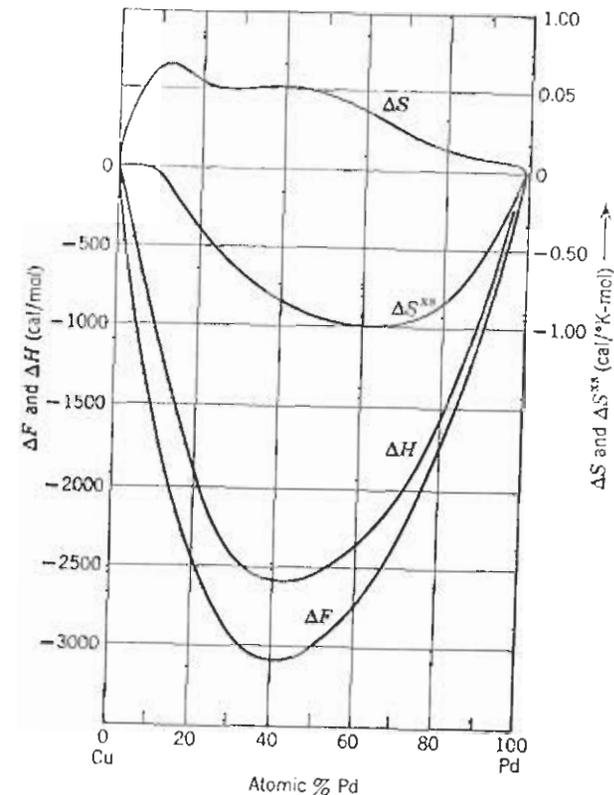


Fig. 7.3 Thermodynamic functions in the Cu-Pd system at 1000°K. Based on Hultgren et al., *Selected Values of Thermodynamic Properties of Metals and Alloys*, Wiley, New York, 1963.

According to this pair potential or quasicheical model, in view of the fact that the enthalpy of interaction of solute-solvent pairs is different from solvent-solvent and solute-solute pairs, a type of ordering will occur which minimizes the free energy of the system. There will be a trade-off, therefore, between the entropy which has a maximum value for complete randomness and the enthalpy which will have a minimum value for an ordered system. For some systems, particularly those that involve transition metals, other factors due to magnetic and electronic effects must be considered.

In order to illustrate the pair potential approach consider an alloy which contains N_A atoms of type A and N_B atoms of type B. There will be three types of interactions to consider, namely, A-A, A-B, and B-B. Each of these will be considered to have associated with it a mean potential H_{AA} ,

H_{AB} , and H_{BB} , respectively. The mean potential refers to the potential between pairs in the close-packed array in solution. This potential is different from that for two atoms, say, in a diatomic molecule. There is in fact no unique potential between a given A and B atom, but rather the value depends upon the environment. Parentheses will be employed (B-A) when the total of A-B and B-A pairs is implied. In a solution which contains N ions, there will be P_{AA} pairs of type A-A, $P_{(AB)}$ pairs of type A-B, and P_{BB} pairs of type B-B. Thus the enthalpy of the solution will be given by

$$H = P_{AA}H_{AA} + P_{(AB)}H_{AB} + P_{BB}H_{BB} \quad (7.1)$$

The next step is to evaluate P_{AA} , $P_{(AB)}$, and P_{BB} . Before attempting this, the treatment may be simplified by elimination of P_{AA} and P_{BB} as follows. The crystal contains N_A atoms of type A and each one of these has Z neighbors where Z is the coordination number. Each A-B pair contains one ion of type A, whereas each A-A bond contains two ions of type A. Further, each ion is shared among Z bonds; thus the number of ions of type A involved in A-B pairs is $P_{(AB)}/Z$ and the number in type A-A pairs is $2P_{AA}/Z$. Since there are N_A atoms of type A,

$$N_A = \frac{P_{(AB)}}{Z} + \frac{2P_{AA}}{Z} \quad (7.2)$$

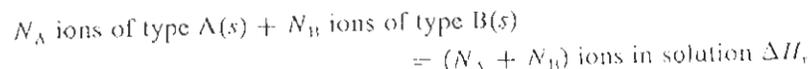
Similarly for type B ions

$$N_B = \frac{P_{(AB)}}{Z} + \frac{2P_{BB}}{Z} \quad (7.3)$$

Thus $P_{AA} + P_{BB}$ can be expressed in terms of $P_{(AB)}$, N_A , N_B , and Z , and substituting into equation 7.1

$$H = \frac{1}{2}ZN_A H_{AA} + \frac{1}{2}ZN_B H_{BB} + P_{(AB)}[H_{AB} - \frac{1}{2}(H_{AA} + H_{BB})] \quad (7.4)$$

We are interested in knowing the heat of mixing, ΔH_m . This is given by the reaction



and

$$\begin{aligned} \Delta H_m &= H - H_A(N_A \text{ ions of type A, pure}) - H_B(N_B \text{ ions of type B, pure}) \\ \Delta H_m &= H - \text{enthalpy of pure A} - \text{enthalpy of pure B} \end{aligned} \quad (7.5)$$

The enthalpies of pure element A and pure element B are given by $\frac{1}{2}Z_A H_{AA}'$ and $\frac{1}{2}Z_B H_{BB}'$, respectively. Z_A and Z_B are the coordination number of the pure elements, respectively, and H_{AA}' and H_{BB}' are the appropriate mean potentials. For the sake of illustration consider $Z_A = Z_B = Z$ and let us

make the assumption that H_{AA} , H_{BB} , and H_{AB} are independent of concentration. Thus H_{BB} in this crude approximation is the same in pure B as when B is a dilute solute in A. This would have only approximate validity when A and B are closely related chemically. If these assumptions are made we find that

$$\Delta H_m = P_{(AB)}[H_{AB} - \frac{1}{2}(H_{AA} + H_{BB})] \quad (7.6)$$

A quantity Ω is defined as

$$\Omega \equiv ZN_0[H_{AB} - \frac{1}{2}(H_{AA} + H_{BB})] \quad (7.7)$$

7.2 APPLICATION TO IDEAL AND REGULAR SOLUTIONS

For an ideal solution $\Delta H_m = 0$; therefore from equation 7.7

$$\Omega = 0 \quad \text{and} \quad H_{AB} = \frac{1}{2}(H_{AA} + H_{BB})$$

We see that a solution will behave ideally if the enthalpy between unlike pairs is the arithmetic average of the enthalpies between like pairs.

In the case of a regular solution it will be recalled that $\Delta H_m \neq 0$ but $\Delta S_m^{reg} = 0$. This latter restriction implies that the vibrational entropy of elements remains unchanged upon transferring from the pure state to the solution and further that the mixing is completely random. As a result, $P_{(AB)}$ can be readily evaluated from simple statistical considerations. Let us consider a gram-atom of alloy. Thus $(N_A + N_B) = N_0$ and $X_A = N_A/N_0$ and $X_B = N_B/N_0$. The probability that an ion of type A will be on a given site is X_A . The probability that an ion of type B will be on a particular nearest neighbor site is X_B and the probability that both will be on their respective sites simultaneously is $X_A X_B$. Similarly, the probability that an atom of type B will be on the former site is X_B and the probability that an atom of type A will be on the latter site is X_A . The probability that they will be on their respective sites simultaneously is again $X_B X_A$. As a result the probability that two sites will be occupied by unlike atoms will be the sum, or $2X_A X_B$. The total number of pairs in the crystal is $\frac{1}{2}ZN_0$, therefore the number of A-B pairs will be equal to the total number of pairs multiplied by the probability that a pair will be of the A-B type. Thus

$$P_{(AB)} = 2X_A X_B \cdot \frac{1}{2}ZN_0 = X_A X_B ZN_0 \quad (7.8)$$

We find therefore that the heat of mixing is

$$\Delta H_m = X_A X_B \Omega \quad (7.9)$$

Since Ω is independent of composition according to the zeroth order approximation, ΔH_m is a parabolic function of composition.

If there is an attractive interaction between unlike ions the A B pair enthalpy will be more negative than the A A pair enthalpy or B B pair enthalpy, and hence Ω will be negative in sign, yielding a negative value of the heat of mixing. Conversely if there is a repulsive interaction between unlike atoms, Ω will be positive and ΔH_m will also be positive.

If a strong attractive interaction between unlike atoms exists, ΔH_m can be made more negative by having short-range order in the solution, which means *increasing* P_{AB} over the random value. This will tend to make the free energy of the solution more negative through reduction of the ΔH_m term. On the other hand, however, the mixing entropy will *decrease*, since \mathcal{W} , the number of ways of arranging atoms on the lattice, is less and thus increases the free energy. (This will be discussed more fully in a later section.) An optimum value of *short-range order* will be attained, reflecting a balance between ΔH_m and the $T\Delta S_m$ contribution. In the case of a repulsive interaction, ΔH_m could be reduced by promoting clustering of like atoms or *decreasing* P_{AB} compared with the random value. This, also, will result in a decrease in \mathcal{W} , the number of ways of arranging atoms on the lattice, and hence a decrease in ΔS_m . Again an optimum degree of *clustering* will result, reflecting a balance between ΔH_m and ΔS_m in order to minimize ΔG_m . The system can achieve a maximum ΔS_m and hence a maximum $T\Delta S_m$ contribution to ΔG_m by the destruction of order, but at the expense of the ΔH_m term, which would be minimum for an ordered system. Because in the expression

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

the ΔS_m term is multiplied by T , the $T\Delta S_m$ term will be more important at elevated temperatures. As a result the degree of ordering or clustering in a system will decrease as the temperature is elevated.

From this discussion it is evident that a regular solution for which $\Delta S_m^{xs} = 0$ will be found only at elevated temperatures in systems where Ω is a small quantity.

We may find $\Delta\bar{H}_A$ and $\Delta\bar{H}_B$, the relative partial molal enthalpies for a regular solution, from equation 7.9 by use of relations derived in Chapter 6.

$$\bar{H}_A - H_A^* = \Delta\bar{H}_A = (1 - X_A)^2\Omega \quad (7.10)$$

$$\bar{H}_B - H_B^* = \Delta\bar{H}_B = (1 - X_B)^2\Omega \quad (7.11)$$

Since $\Delta S^{xs} = 0$,

$$\bar{S}_A - S_A^* = \Delta\bar{S}_A = -R \ln X_A$$

$$\bar{S}_B - S_B^* = \Delta\bar{S}_B = -R \ln X_B$$

Using the relation

$$\Delta\bar{G}_i = \Delta\bar{H}_i - T\Delta\bar{S}_i$$

7.2 Application to Ideal and Regular Solutions

we find that

$$\Delta\bar{G}_A = (1 - X_A)^2\Omega + RT \ln X_A = RT \ln a_A$$

$$\Delta\bar{G}_B = (1 - X_B)^2\Omega + RT \ln X_B = RT \ln a_B$$

We see that

$$\ln \gamma_A = \frac{(1 - X_A)^2\Omega}{RT} \quad (7.12)$$

$$\ln \gamma_B = \frac{(1 - X_B)^2\Omega}{RT} \quad (7.13)$$

Thus for a regular solution, the activity coefficient is strongly related to the interaction parameter, Ω . As will be shown later, γ_i for a nonregular solution is also a function of ΔS_i^{xs} .

When the interaction between unlike atoms is attractive, Ω is negative, and hence $\ln \gamma_i$ is negative and $\gamma_i < 1$, giving negative deviation from Raoult's law. Conversely, when Ω is positive, $\gamma_i > 1$, giving positive deviation from Raoult's law. In Fig. 7.4 are shown values of ΔG_m at 1000°K, as a function of composition for various values of Ω . It is observed that the function is symmetric about $X_A = X_B = 0.5$. In Fig. 7.5 are shown values of a_A as a function of composition, and Ω at 1000°K as calculated from Fig. 7.4. From the equations derived, it may be seen that Henry's law is only an

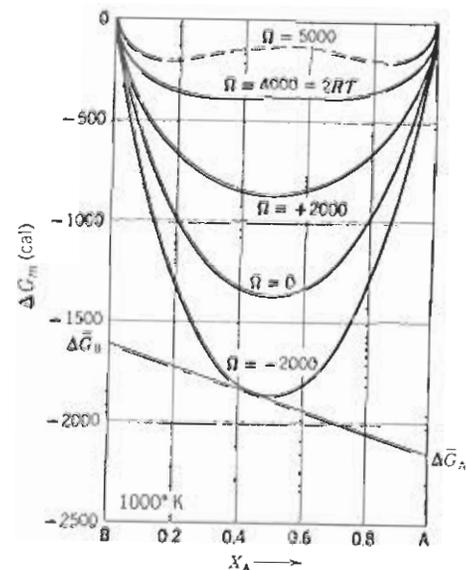


Fig. 7.4 Heat of mixing as a function of composition for a regular solution for various values of Ω . From O. J. Kleppa, in *Liquid Metals and Solidification*, ASM, Cleveland, 1958.