

### Magnetic Order

For a pure component in which the atoms have magnetic moments, or for an alloy in which at least one component has a magnetic moment, order-disorder theory may be applied to the ordering of spins.<sup>1</sup> A paramagnetic material corresponds to a disordered array of spins whereas the ferromagnetic, antiferromagnetic, or ferrimagnetic states correspond to an ordered assembly. The transformation from an ordered state to a disordered state is usually found to be second-order, as discussed earlier, and has a magnetization-temperature curve as illustrated in Fig. 7.15. One therefore observes a discontinuity in the heat capacity versus temperature curve.

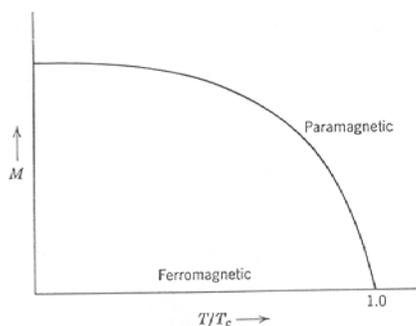


Fig. 7.15 Magnetization versus reduced temperature for a ferromagnetic-paramagnetic transition.  $T_c$  is the Curie temperature.

For an alloy A-B in which A has a magnetic moment  $\mu_A^{\text{alloy}}$  and B a moment  $\mu_B^{\text{alloy}}$ , the entropy of mixing associated with the mixing of moments alone is calculated to be<sup>2</sup>

$$\Delta S_m(\text{mag}) = R[\ln(\mu_A^{\text{alloy}} + 1) + \ln(\mu_B^{\text{alloy}} + 1) - X_A \ln(\mu_A + 1) - X_B \ln(\mu_B + 1)] \quad (7.27)$$

where  $\mu_A$  and  $\mu_B$  are the moments in pure A and B, respectively.

### 7.5 SOME GENERAL CONSIDERATIONS OF ALLOY SYSTEMS

In a general sense the thermodynamics properties of an alloy will be the sum of several contributions. The configurational contribution has been

<sup>1</sup> H. Sato, in *Physical Chemistry—An Advanced Treatise*, Vol. X, W. Jost, Ed., Academic Press, New York, 1970.

<sup>2</sup> R. Weiss and P. Tauer, *Phys. Rev.*, **102**, 1490 (1956).

discussed at some length in this chapter. In addition there are electronic contributions, magnetic contributions (discussed above), and vibrational contributions. The entropy of mixing, therefore, may in principle be equal to the sum of these four contributions.

$$\Delta S_m^{\text{xs}} = \Delta S_{\text{cont}}^{\text{xs}} + \Delta S_{\text{mag}} + \Delta S_{\text{vib}} + \Delta S_{\text{el}}$$

Excess symbols are left off three of the terms since they all represent excess contributions.

The magnetic and electronic contributions may be very important in alloys which involve one or more transition metals whereas the configurational and vibrational terms are generally present. An approximate equation for  $\Delta S_{\text{vib}}$  at high temperatures may be readily derived.

Let us consider the vibrational entropy contribution to a crystal at elevated temperatures. For this situation most frequencies are close to  $\nu_m$ . Consequently, it will be a reasonable approximation to use the Einstein approach. As we have shown earlier the entropy of an oscillator is given by

$$S = k \ln \mathcal{Z} + kT \left( \frac{\partial \ln \mathcal{Z}}{\partial T} \right)_V$$

where

$$\mathcal{Z} = \frac{\exp(-h\nu/2kT)}{1 - \exp(-h\nu/kT)}$$

Expanding  $\mathcal{Z}$  in an infinite series,

$$\mathcal{Z} = \frac{1 - (h\nu/2kT) + \frac{1}{2}(h\nu/2kT)^2 + \dots}{(h\nu/kT) - \frac{1}{2}(h\nu/kT)^2 + \dots}$$

At high temperatures  $h\nu/kT \ll 1$ , and hence high-order terms in the infinite series may be neglected. Thus

$$\mathcal{Z} \cong \frac{kT}{h\nu}$$

Assuming  $\nu$  to be independent of temperature at high temperatures, the vibrational entropy per oscillator is found by substitution to be:

$$S_v = k \left( \ln \frac{kT}{h\nu} + 1 \right)$$

Since a gram-atom of crystal has  $3N$  oscillators, the entropy per gram-atom is

$$S_v = 3R \left( \ln \frac{kT}{h\nu} + 1 \right) \quad (7.28)$$

Suppose now that the oscillators are changed from frequency  $\nu$  to  $\nu'$ . The entropy change associated with this process is

$$\Delta S_\nu = 3R \ln \left( \frac{\nu}{\nu'} \right)$$

Thus if the frequency is lowered,  $\Delta S_\nu$  will be positive.

Consider equation 7.28 in the case of alloy formation

$$X_A \text{ (pure A)} + X_B \text{ (pure B)} = \text{Alloy } (X_A, X_B)$$

The Debye frequency of pure A is  $\nu_A$ , of pure B is  $\nu_B$ , and of the alloy is  $\nu_D$ . Therefore

$$\Delta S_\nu = 3R \ln \left( \frac{\nu_A^{X_A} \cdot \nu_B^{X_B}}{\nu_D} \right)$$

and since the Debye temperature  $\theta$  is equal to  $\ln \nu/k$

$$\Delta S_\nu = 3R \ln \frac{\theta_A^{X_A} \cdot \theta_B^{X_B}}{\theta}$$

Consequently, the vibrational contribution to the entropy of mixing may be estimated if the relevant Debye temperatures are known.

The electronic contribution  $\Delta S_{el}$  at high temperature may be estimated from the low-temperature heat capacity,  $\gamma$ . It will be recalled that the heat capacity at very low temperatures is due to absorption of energy by electrons near the Fermi surface. On the basis of rigid band calculations

$$N(U) = \frac{3\gamma}{2\pi^2 k^2}$$

where  $N(U)$  is the electron density of states. For an alloy containing a transition metal,  $\gamma$  and thus  $N(U)$  may vary considerably with composition, as shown in Fig. 7.16 for the Cu-Pd system.

If the rigid band theory is employed the electronic entropy contribution is given by

$$S_{el} = \int_0^T \gamma dT = \gamma T$$

or for the formation of an alloy

$$\Delta S_{el} = [\gamma_{\text{alloy}} - (X_A \gamma_A + X_B \gamma_B)]T$$

where  $\gamma_A$  and  $\gamma_B$  are the values for the pure components.

For any given alloy  $\Delta S_{mi}^{xs}$  would normally be dominated by one or two of these four contributions. Calculations for the Cu-Pd system are shown in Fig. 7.17. Comparison with Fig. 7.3 shows rather good agreement with thermodynamic data.

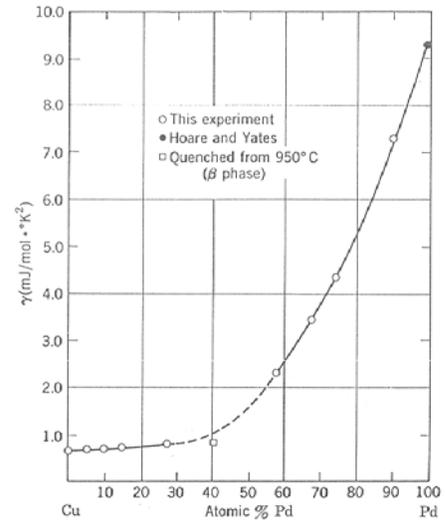


Fig. 7.16 The dependence of  $\gamma$  on composition in the Cu-Pd system. From Y. Sato, J. M. Sivertsen, and L. E. Toth, *Phys. Rev.* B1, 1402 (1970).

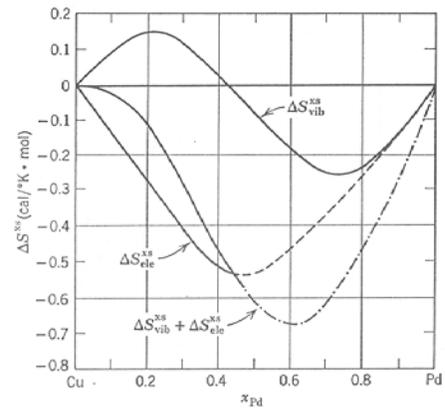


Fig. 7.17 Excess vibrational and electron entropies at 1000°K as calculated from  $\theta$  and  $\gamma$  values. From Y. Sato, J. M. Sivertsen, and L. E. Toth, *Phys. Rev.*, B1, 1402 (1970).

The electronic contribution to the energy term may be simply obtained from the  $\gamma$  quantities if available.

$$\Delta U_{e1} = \int_0^{X_A} \frac{dX_A}{N(U)} = \frac{2\pi^2 k^2}{3} \int_0^{X_A} \frac{dX_A}{\gamma}$$

This term is calculated to be as large as  $-15$  kJ/mol in the Cu-Pd system and would not be counted in a calculation based on pair potential concepts. Thus the degree of short-range order would be overestimated from thermodynamic data if all of the large value of  $\Delta H_m$  shown in Fig. 7.3 was ascribed to the  $[u + j(X)]$  term and  $\Delta U_{e1}$  was not removed from  $\Delta H_m$  before calculation.

#### PROBLEMS

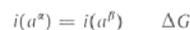
1. In a face-centered cubic lattice containing 40 at % A and 60 at % B in the form of a random solution, calculate the number of A-A pairs, B-B pairs, and A-B pairs in a gram-atom of solution.
2. An f.c.c. alloy of composition 40% A and 60% B shows substantial short-range order.  $P_{AB}$  is found from x-ray measurements to be 1.05 times the value for a random solution. Calculate  $P_{AA}$  and  $P_{BB}$  in a gram-atom of alloy.
3. For Problem 2 calculate the configurational entropy of mixing. Calculate the excess configurational entropy of mixing. Calculate the enthalpy of mixing and the excess free energy of mixing, assuming that the thermodynamic properties are governed by the configurational contribution.
4. For the Cu-Pd system, calculate the electronic contribution to the energy of mixing. Estimate the difference between the enthalpy of mixing and energy of mixing. With a negative heat of mixing as shown in Fig. 7.3, would it be possible to have clustering instead of short-range order?
5. Supposing that the short-range order parameter in a 50% Cu, 50% Pd is equal to 0.04, calculate the excess configurational entropy. Compare with  $\Delta S_v$  and  $\Delta S_{e1}$  presented in Fig. 7.17.
6. Calculate the maximum value of the long-range order parameter in an f.c.c. alloy which contains 15% A and 85% B.

## Equilibrium Between Phases of Variable Composition

### 8.1 GIBBS PHASE RULE

In this chapter we shall show how, in special cases, useful thermodynamic data may be obtained directly from phase diagrams. In addition the relation of extent of solubility upon factors such as external pressure and particle size will be investigated. Before examining these topics some consideration should be given to the *Gibbs phase rule*. This rule, presented by J. W. Gibbs in four pages of a paper which had a total length of 130 pages, has had a significant influence on phase diagram construction and the relationship between phases. It is ironic that, although the paper was published in 1876, it wasn't until about the year 1900 that its importance was recognized. Prior to 1900, many published phase diagrams were fundamentally incorrect and the phase rule provided useful rules about the construction of these diagrams. Before deriving the phase rule let us consider one important property of  $\bar{G}_i$  when component  $i$  is present in different phases. For simplicity let us consider two phases. The arguments, however, may be readily extended to more than two phases.

Consider very large amounts of two phases, both of which contain component  $i$  as shown in Fig. 8.1. Component  $i$  in the  $\alpha$  phase will have an activity  $a_i^\alpha$ , and in the  $\beta$  phase it will have an activity  $a_i^\beta$ . Let us transfer a gram-atom of  $i$  from  $\alpha$  to  $\beta$  at a constant temperature without changing composition. The original quantities of  $\alpha$  and  $\beta$  are so large that the composition is changed only infinitesimally. The reaction is



Component  $i$  in  $\beta$  will have a partial molar free energy given by

$$\bar{G}_i^\beta = G_i^\circ + RT \ln a_i^\beta$$