The Evolution of Solutions: A Thermodynamic Analysis of Mechanical Alloying

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Normal thermodynamic theory for solutions begins with the mixing of component atoms. Many solutions are, however, prepared by mixing together lumps of the components, each of which might contain millions of identical atoms. We examine here the way in which a solution evolves from these large clusters of components, from a purely thermodynamic point of view. There are some interesting results, including the prediction that solution formation by the mechanical alloying of solid components cannot occur unless there is a gain in coherency as the particles become small. The nature of the barrier to mechanical alloying is discovered. There is also the possibility of a metastable state prior to the achievement of full solution, when the component atoms prefer like-neighbors.

I. INTRODUCTION

CONSIDER the pure components A and B with molar free energies μ_A° and μ_B°, respectively. If the components are initially in the form of powders, then the average free energy of mixture of such powders is given by

$$G\{\text{mixture}\} = (1 - x)\mu_A^\circ + x\mu_B^\circ \qquad [1]$$

where x is the mole fraction of B. It is assumed that the powder particles are so large that the A and B atoms do not ''feel'' each other's presence *via* interatomic forces between unlike atoms. It is also assumed that the number of ways in which the mixture of powder particles can be arranged is not sufficiently different from unity to give a significant contribution to a configurational entropy of mixing. Thus, a blend of powders that obeys Eq. [1] is called a *mechanical mixture*. It has a free energy that is simply a weighted mean of the components, as illustrated by the point u in Figure 1 for a mean composition x.

A solution, on the other hand, describes a mixture of atoms or molecules, *i.e.*, the smallest particle in the present context since mixing cannot be achieved on an even finer scale. Generally, there will be an enthalpy change associated with the change in near-neighbor bonds. Because the total number of ways in which the ''particles'' can arrange is now very large, there will always be a significant contribution from the entropy of mixing. The free energy of the solution is therefore different from that of the mechanical mixture, as illustrated by point v in Figure 1. The difference in the free energy between these two states of the components is the free energy of mixing, the essential term in all thermodynamic models for solutions.

In practice, many solutions do not form instantaneously from a mixture of large particles to an intimate mixture of atoms. Instead, the system must go through a series of transition states involving ever decreasing particle sizes and increasing number densities as the particles are subdivided. One example is the process of mechanical alloying[1] in which a mixture of large particles is attrited until the subdivision of particles ultimately leads to the formation of a solution. The violent mixing of two initially immiscible liquids is another example. The aim of the work presented here is to study this evolution of such solutions from a purely thermodynamic point of view. It has never been clear as to when the component powders in mechanical alloying become more like a solution than a mechanical mixture.

II. THERMODYNAMIC ANALYSIS

We consider a binary system consisting of pure components A and B. In contrast to the conventional approach for solution theory, the equation for the free energy of mixing must contain particle sizes that can be much greater than an atom.

A. *Configurational Entropy*

The change in configurational entropy as a consequence of mixing can be obtained using the Boltzmann equation $S = k \ln \{w\}$, where w is the number of configurations and k has its usual meaning.

Suppose that there are m_A atoms per powder particle of A and m_B atoms per particle of B; the powders are then mixed in a proportion that gives an average concentration of B, which is the mole fraction x.

There is only one configuration when the heaps of pure powders are separate. When the powders are randomly mixed, the number of possible configurations for a mole of atoms becomes

$$\frac{(N_a([1 - x]/m_B + x/m_A))!}{(N_a[1 - x]/m_A)!\ (N_a x/m_B)!} \qquad [2]$$

The numerator in eq. [2] is the total number of particles and the denominator the product of the factorials of the A and B particles, respectively. Using Stirling's approximation, we obtain the molar entropy of mixing as

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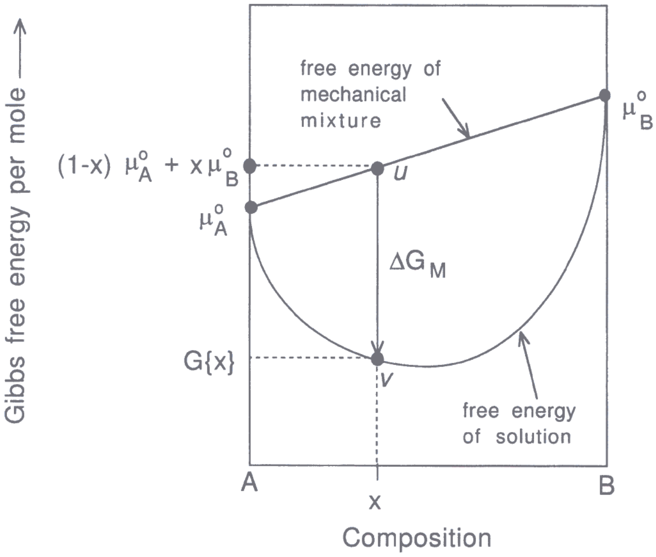

Fig. 1—Plot of the molar Gibbs free energy *vs* composition (mole fraction), both for mechanical mixtures and for solutions. $G\{x\}$ is the free energy of the solution of composition x, whereas $(1 - x)\mu_A^\circ + x\mu_B^\circ$ is the free energy of the corresponding mechanical mixture of large particles of A and B.

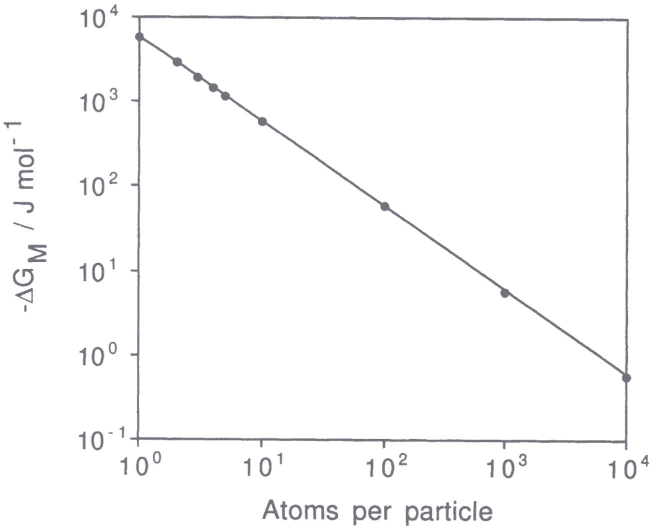

Fig. 2—The molar Gibbs free energy of mixing, $\Delta G_M = -T\Delta S_M$, for a binary alloy, as a function of the particle size when all the particles are of uniform size in a mixture whose average composition is equiatomic. T = 1000 K.

$$\frac{\Delta S_M}{kN_a} = \frac{(1-x)m_B + xm_A}{m_A m_B} \ln \left\{N_a \frac{(1-x)m_B + xm_A}{m_A m_B}\right\} - \frac{1-x}{m_A} \ln \left\{\frac{N_a(1-x)}{m_A}\right\} - \frac{x}{m_B} \ln \left\{\frac{N_a x}{m_B}\right\} \qquad [3]$$

subject to the condition that the number of particles remains integral and nonzero. As a check, it is easy to show that this equation reduces to the familiar

$$\Delta S_M = -kN_a\,[(1-x)\ln\{1-x\} + x\ln\{x\}]$$

when $m_A = m_B = 1$.

Naturally, the largest reduction in free energy occurs when the particle sizes are atomic. This is illustrated in Figure 2, which shows the molar free energy of mixing for a case where the average composition is equiatomic, assuming that only configurational entropy contributes to the free energy of mixing. An equiatomic composition maximizes configurational entropy. When it is considered that phase changes often occur at appreciable rates when the accompanying reduction in free energy is just 10 J mol^{-1}, Figure 2 shows that the entropy of mixing cannot be ignored when the particle size is less than a few hundred atoms. In commercial practice, powder metallurgically produced particles are typically 100 μm in size, in which case the entropy of mixing can be neglected entirely, though solution formation must be considered to be advanced when the processing reduces particle dimensions to some 10^2 atoms. These comments must be qualified by the fact that we have neglected any enthalpy changes, which are treated in Section B.

B. *Enthalpy*

A major component of the excess enthalpy of mixing comes from the fact that there will be, in most cases, a change in the energy when new kinds of bonds are created during the formation of a solution.

In the regular solution model, the enthalpy of mixing is obtained by counting the different kinds of near-neighbor bonds when the atoms are mixed at random. This information, together with the binding energies, gives the required change in enthalpy on mixing. The binding energy may be defined by considering the change in energy as the distance between a pair of atoms is decreased from infinity to an equilibrium separation. The change in energy during this process is the binding energy, which, for a pair of A atoms, is written $-2\varepsilon_{AA}$. It follows that when $\varepsilon_{AA} + \varepsilon_{BB} < 2\varepsilon_{AB}$, the solution will have a larger than random probability of bonds between unlike atoms. The converse is true when $\varepsilon_{AA} + \varepsilon_{BB} > 2\varepsilon_{AB}$, since atoms then prefer to be neighbors to their own kind.

With the approximation that atoms in a solution are randomly dispersed, the number of A-A bonds in a mole of solution is $zN_a(1-x)^2$, B-B bonds $zN_a x^2$, and A-B bonds $2zN_a(1-x)x$, where z is the coordination number. It follows that the molar enthalpy of mixing is given by

$$\Delta H_M \simeq N_a z(1-x)xw \qquad [4]$$

where

$$w = \varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB} \qquad [5]$$

The product $zN_a w$ is often called the regular solution parameter, which we shall label Ω in the subsequent discussion.

This treatment of the enthalpy of mixing has to be adapted for particles that are not monoatomic. For example, only those atoms at the interface between the A and B particles will feel the influence of the unlike atoms. Assuming cubic particles, each of volume V_i and surface area $S = 6(V_i)^{2/3}$, we have

$$V_i = m_i \Phi_i \text{ and } V_T = \sum_i \frac{N_a x_i}{m_i} V_i$$

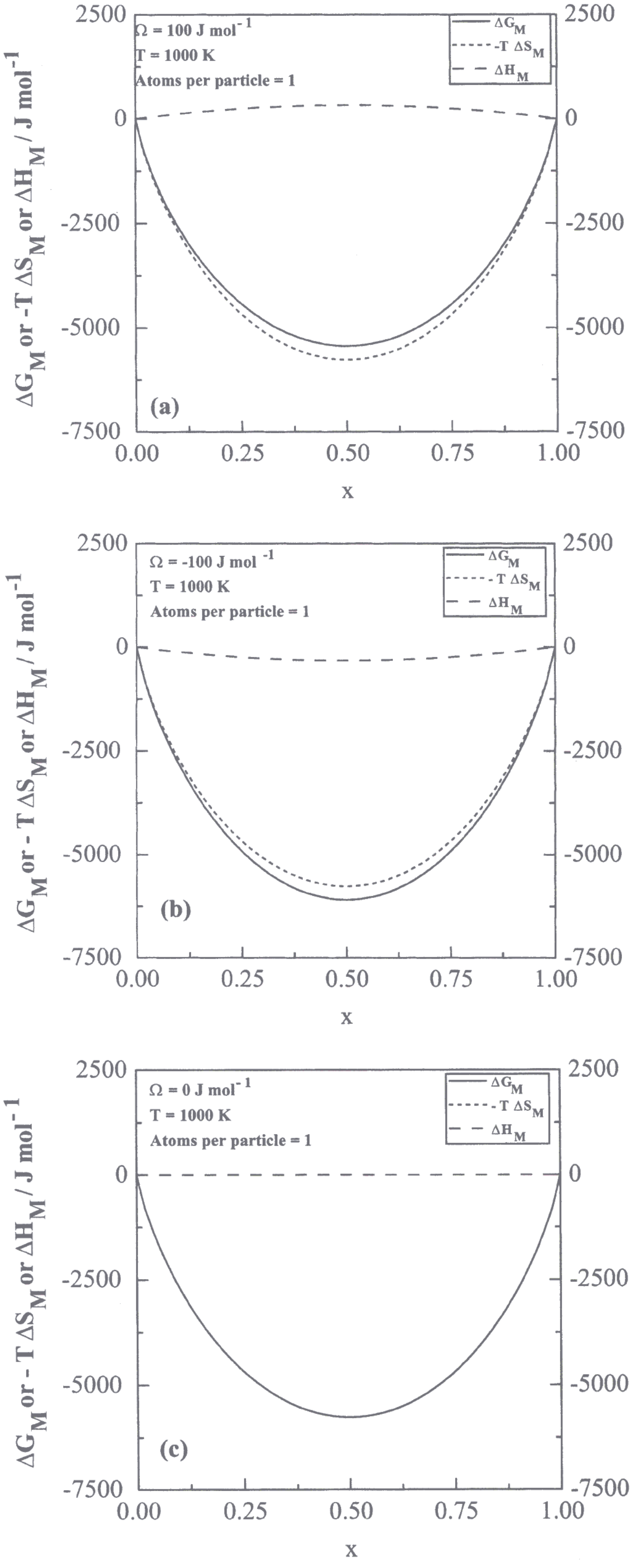

Fig. 3—Plots of the free energy, entropy, and enthalpy of mixing in a binary system at 1000 K. (*a*) $\Omega = 100$ J mol^{-1}, (*b*) $\Omega = -100$ J mol^{-1}, and (*c*) $\Omega = 0$ J mol^{-1}..

where the subscript *i* represents the component, Φ_i is the volume per atom, x_i is the mole fraction, V_T is the total volume, and N_a is Avogadro's number.

The total surface area of n_i isolated particles is $S_T = \Sigma_i n_i S$ but the total grain boundary area when the particles are compacted is half this value. It follows that the grain boundary area per unit volume, S_V is given by

$$S_V = \left(\frac{1}{2}\sum_i n_i 6(m_i\Phi_i)^{2/3}\right) \Big/ \left(\sum_i \frac{N_a x_i}{m_i} V_i\right) \qquad [6]$$

If it is assumed that the boundary has a thickness 2δ (two monolayers), then the volume fraction of material within the boundary is $S_V \times 2\delta$. The enthalpy of mixing can only be generated within this region where the unlike atoms meet. It follows that

$$\Delta H_M = \Omega\ 2\delta S_V\ x(1 - x) \qquad [7]$$

C. *Interfacial Energy*

The role of the interface as discussed in Section B is simply to identify the number of different atoms that are physically close enough to interact. However, there is a further term that must be taken into account, which does not occur in conventional solution theory. This comes from the inevitable disorder present at the interface, giving a structural component of the interfacial energy as σ per unit area. The chemical component of interfacial energy is already included in the enthalpy of mixing term. The net cost due to the structural component is

$$\Delta H_I = V_m S_V \sigma \qquad [8]$$

where V_m is the molar volume.

The term ΔH_I is the *change* in enthalpy content due to interfaces. It is assumed that $S_V \simeq 0$ for very large particles. The process is envisaged as one in which the very large particles are reduced to smaller ones on the route toward the formation of a solution. This is a reasonable description of the mechanical alloying process. It is also assumed in this analysis that σ is identical for interfaces between *A-A* particles, *B-B* particles, and *A-B* particles.

III. RESULTS AND DISCUSSION

The modeling of atomic solutions is well established, but Figure 3 nevertheless presents the results for particles that are 1 atom in size. This is to illustrate the magnitude of the free energy changes involved for comparison against later results and to highlight the fact that the energy of mixing is zero for the pure components. There are three cases illustrated corresponding to solutions in which like atoms tend to cluster ($\Omega > 0$), those in which they tend to order ($\Omega < 0$), and the ideal solution ($\Omega = 0$). The calculations are for 1000 K, the temperature dependence appearing only *via* the ($-T\Delta S_M$) term. Finally, interfacial energy does not feature in these plots, because the solution is atomic and therefore fully coherent.

Difficulties arise when considering the evolution of a solution from a mixture of large particles to mixtures with ever decreasing sizes. This scenario precisely describes mechanical alloying, where the component powders are repeatedly fractured and deformed until an atomic solid solution is formed. The refinement of particle size leads to an increase in the amount of interface per unit volume (S_V). If the interface energy is constant, then the cost indicated

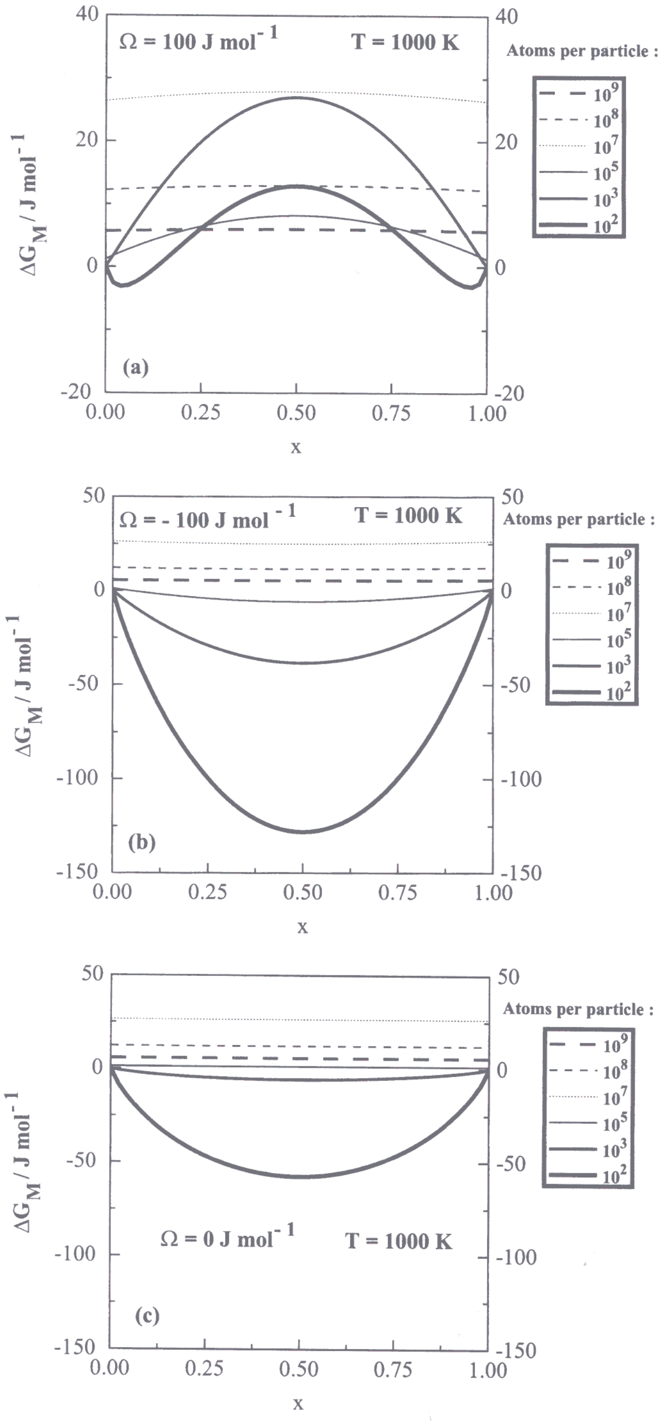

Fig. 4—Plots of the free energy of mixing in a binary system at 1000 K, as a function of the number of atoms in the particles. (*a*) $\Omega = 100$ J mol^{-1}, (*b*) $\Omega = -100$ J mol^{-1}, and (*c*) $\Omega = 0$ J mol^{-1}.

by Eq. [8] must eventually overwhelm any advantage from the entropy or enthalpy of mixing. The inescapable conclusion is that mechanical alloying cannot occur unless there is a gain in coherency, *i.e.*, a reduction in the interfacial energy as atomic dimensions are approached. This is not surprising in hindsight, since the process envisaged is the opposite of the normal precipitation and growth event, in which a small particle begins coherently and loses coherency as it grows.

Since the change in the interfacial energy with particle size is not known, we have assumed that σ remains constant until a size of 10^7 atoms is reached. Beyond that, the energy decreases linearly to zero when the particle size is 1 atom:

$$\begin{aligned} \sigma &= 0.5 \text{ J m}^{-2} && m > 10^7 \text{ atoms per particle} \\ \sigma &= 0.5\left(1 - \frac{10^7 - m}{10^7}\right) \text{ J m}^{-2} && m \leq 10^7 \text{ atoms per particle} \end{aligned} \qquad [9]$$

The results as a function of particle size are illustrated in Figure 4. A typical powder particle at the beginning of the mechanical alloying process might be some 10^{17} atoms in size, but the calculations begin at 10^9 in order to see significant effects. The free energy change as the particle size is reduced to 10^9 atoms is, at first, mainly a contribution from the increase in the structural component of interfacial energy. The net free energy change remains positive until contributions from the enthalpy and entropy of mixing begin to become significant and when the interfacial energy term begins to decrease below 10^7 atoms due to a gain in coherency.

The energy changes are all very much smaller than associated with the direct formation of an atomic solution (*cf.* Figure 3). This is because the contribution from configurational entropy is small until the particle size reaches about 100 atoms, and that from enthalpy is small because only those atoms at unlike particle interfaces can interact. The details also depend on the nature of the solution, the sign, and the size of Ω. For the case where like atoms tend to cluster ($\Omega > 0$), a pair of minima develop, in the *A*- and *B*-rich regions, in the ΔG_M function as the particle size is reduced. Solution formation is not favored when the concentrations of the two components are about equal. The opposite is true when $\Omega \geq 0$, and mixing is favored at all compositions once the particle size becomes small enough for coherency to set in.

Figure 5 shows how there is a barrier to the formation of a solid solution during the mechanical alloying process. The barrier occurs for all the examples illustrated because of the incorporation of interfacial energy in the analysis. This dominates in the early stages as the particle size is reduced, until a size is achieved below which coherency begins to set in. It is important to note that when $\Omega > 0$, there is an energy barrier, even in the absence of interfacial energy, since the alloying forces unlike atoms to mix, leading to an increase in enthalpy. Naturally, this latter effect is minimized at low or high concentrations that are A- or B-rich, respectively. Figure 5(a) reveals the possibility that there is an energy well in the curve of energy *vs* particle size, suggesting a possible metastable state making the alloying process particularly difficult. However, the general result is that there is a certain particle size below which mechanical alloying proceeds rapidly with a reduction in free energy.

Finally, the entropy term $-T\Delta S$ ensures that the effect of increasing the temperature is, for all finite *x*, to make the alloying process easier (Figure 6).

IV. CONCLUSIONS

A model has been developed to deal with a situation in which a solution is created by continuously refining a mixture of powder particles of pure components. This process

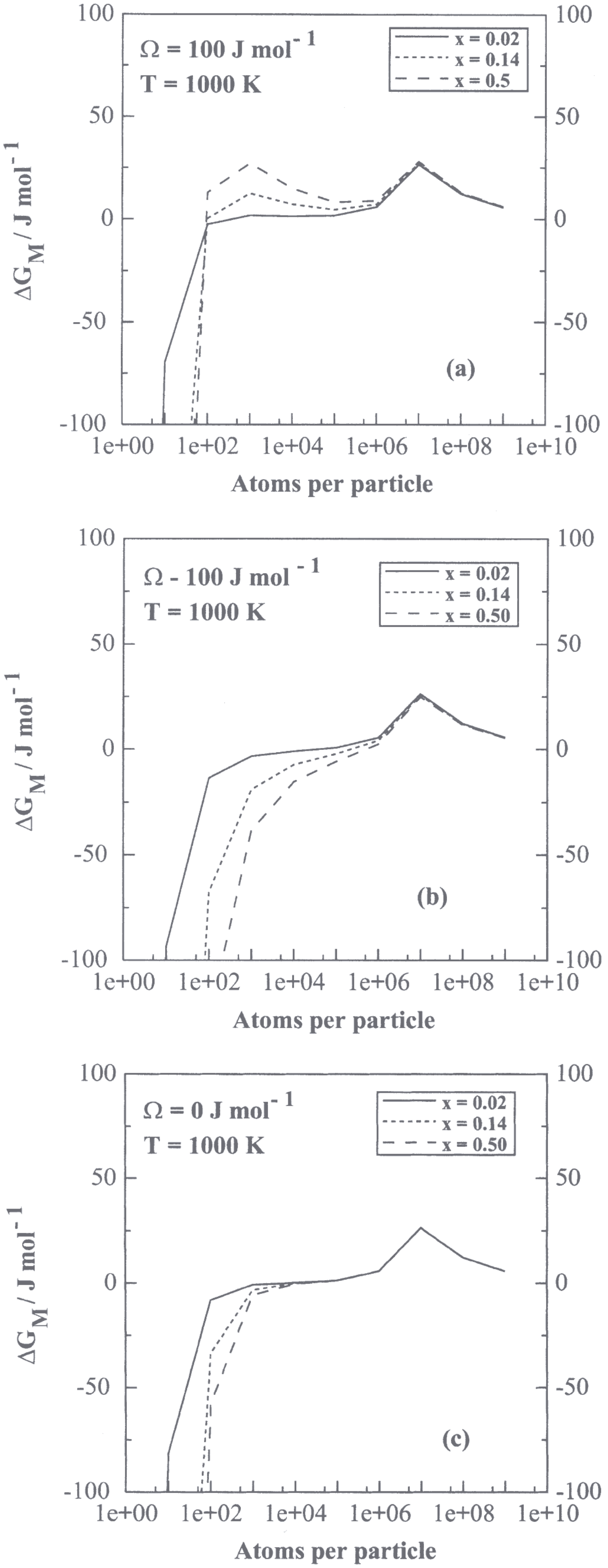

Fig. 5—Free energy *vs* the number of atoms per particle as a function of the concentration at T = 1000 K. (*a*) Ω = 100 J mol^{-1}, (*b*) Ω = −100 J mol^{-1}, and (*c*) Ω = 0 J mol^{-1}. The jagged appearance is because the calculated points have been connected with straight segments. The true variation is expected to be smooth.

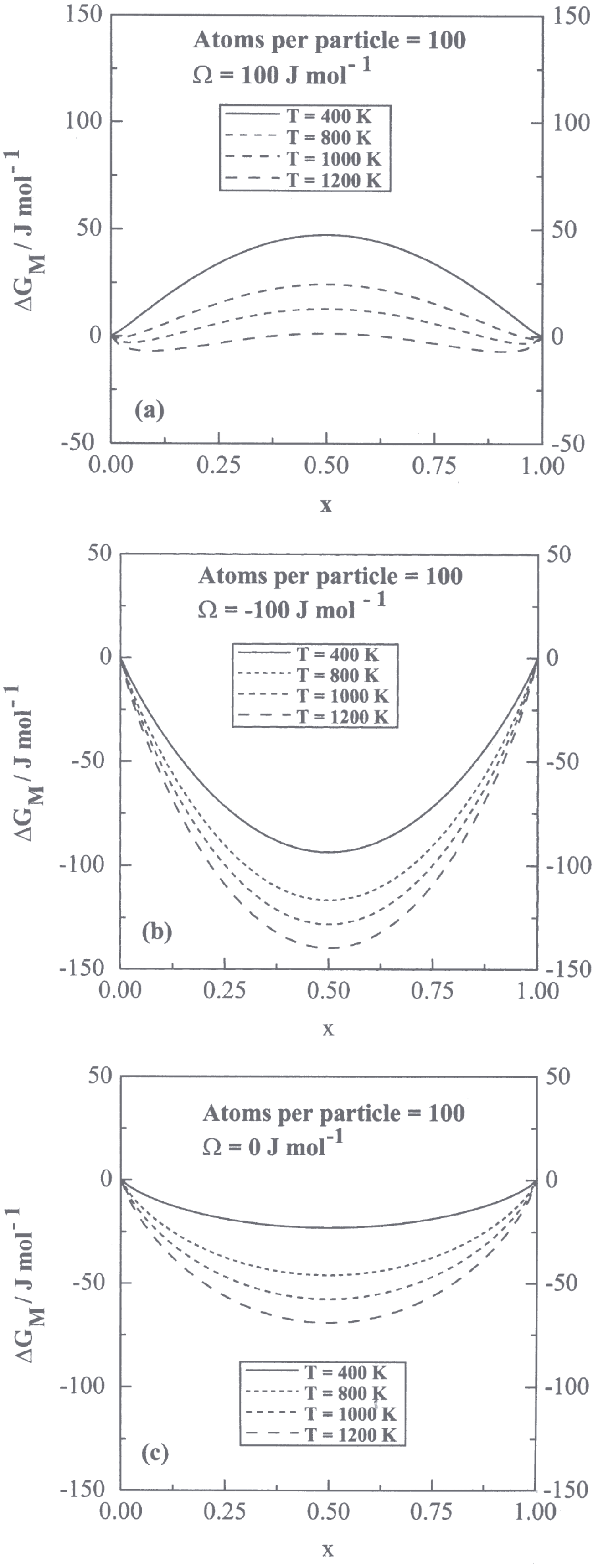

Fig. 6—Effect of temperature on the free energy of mixing for a particular size containing 100 atoms per particle. (*a*) Ω = 100 J mol^{-1}, (*b*) Ω = −100 J mol^{-1}, and (*c*) Ω = 0 J mol^{-1}.

of solution formation is a good representation of the mechanical alloying process.

It is predicted that mechanical alloying is not possible unless initially incoherent interfaces approach coherency and eventually disappear as true solution is approached. The inclusion of interfacial energy also predicts the existence of a barrier to the evolution of the solution. For cases where like atoms tend to cluster, it is possible in principle to obtain a metastable state before solution formation is completed.

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