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Surface Segregation in Alloys: Spheroidal Particles

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Segregation of one component to the surface of a roughly spherical particle is treated in the Bragg–Williams approximation. The number of missing bonds for each atom is considered explicitly and exactly. It is shown that the composition profile may be oscillatory due to this effect. A comparison with thin films is also discussed. For a very small hemispherical particle the occurrence of chemically distinguishable clusters is demonstrated. The effect of the support on the occurrence of these clusters is discussed.

INTRODUCTION

The surface composition of bimetallic catalyst particles is a key factor in the performance of catalysts. Many papers have been published which treat the problem of surface segregation to flat surfaces of fixed crystallographic orientation (*1–7*). In most of these calculations the bulk of the material is supposed to be an infinite source of matter and constraints of mass balance on the surface composition are only occasionally considered (*6, 7*). For small catalytic particles, containing perhaps only a few hundred atoms, both the surface orientation and the mass balance effect have to be considered. Also bonding to the support may influence the surface composition.

In general the distribution of two kinds of atoms in an alloy is determined by the free energy (or Gibbs energy) of the system. Only that particular arrangement is thermodynamically stable which has the lowest free energy. There are two different ways to find this stable configuration. The first and most direct method is to compute the energies E_j of all possible configurations j in which N_A atoms A and N_B atoms B can be arranged in a particle of $N_A + N_B$ atoms. From elementary statistical mechanics the probability of finding a specific configuration j is then

$$P_j = \frac{\omega_j \exp - E_\mathrm{k}/kT}{\sum_i \omega_i \exp - E_i/kT} \qquad (1)$$

where ω_j is the degeneracy of the energy level E_j and the sum is over all possible energy levels. Note that P_j is temperature dependent. At $T = 0$ only the lowest energy configuration occurs (with unit probability), whereas at infinite temperature all possible configurations will occur with probabilities:

$$P_j = \frac{\omega_j}{\sum_i \omega_i}. \qquad (2)$$

If this scheme could be implemented, i.e., if one could find the energy of all possible configurations, the problem would be solved. Unfortunately, this procedure is tractable only for very small systems. The number of configurations for a given number of A and B atoms, $(N_A + N_B)!/(N_A!N_B!)$, rapidly becomes too large to handle. In this paper we restrict our calculations to $N_A = 2$, $N_B = 9$, whence the total number of configurations is 55, and approximate the calculation of the energy levels to include nearest-neighbor interactions only, including the effect of bonding to the carrier material.

A second procedure to arrive at the equilibrium distribution of two types of atoms in

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an alloy is to compute directly the free energy of the system (G) for all configurations of A and B atoms and to determine which of these has the lowest value of G. This involves computing the energy (E) and entropy (S) separately. For slabs, consisting of parallel layers, these quantities are commonly considered to be only a function of the mole fraction of one component in that layer (say $x_A^{(l)}$) but not of the distribution of A and B within the layer.

The quantity to be minimised is then

$$G = \sum_l E_l(x_A^{(l)}) - TS(x_A^{(l)}) \tag{3}$$

subject to the constraint that

$$\sum_l x_A^{(l)} = \text{constant}. \tag{4}$$

Here the summations run over all layers of the slab. The configurations referred to above are now just the mole fractions $x_A^{(l)}$ in a given layer. Assuming that these have been found, it is seen that this procedure yields results of considerably less detail than the previous approach, where the individual probabilities of each specific arrangement of atoms were obtained (Eq. (1)). It is, however, easy to apply to systems with a large number of layers.

As remarked before, the first step in any approach must be the calculation of the energy of a given configuration. In principle this could be done quantum mechanically, but the work involved in accounting for all electrons in even a small cluster is considerable. More empirical methods employ parameters in their wave functions or matrix elements adjusted to specific experimental observations. Instead of doing this we have chosen to work with pair-wise additive bond strengths between two atoms and to restrict the summations necessary to calculate the total energy of the system to nearest neighbors only. For an A–B alloy we then have three parameters, viz. H_{AA}, H_{BB}, and H_{AB} (or $\Omega \equiv H_{AB} - \frac{1}{2}(H_{AA} + H_{BB})$). These are analogous, though not identical, to the parameters β_{AA}, β_{BB}, and β_{AB} which occur in a one-electron Hückel treatment where β_{ij} is the energy overlap integral between neighboring i–j atoms.

The neglect of all but nearest-neighbor interactions may be justified somewhat by considering the interatomic potential to be of the Lennard–Jones type

$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^6}. \tag{5}$$

For an atom in the bulk the total potential is

$$V_{\text{tot}} = \sum_{\mathbf{r}} V(r) \tag{6}$$

where the sum is over all lattice vectors **r**. These sums can be performed for an fcc lattice in terms of the nearest-neighbor distance r_0 with the result

$$V_{\text{tot}} = 12.13\frac{A}{r_0^{12}} - 14.45\frac{B}{r_0^6}. \tag{7}$$

As can be seen, the coefficients are close to 12, the value for nearest neighbors only. It is thus expected that, by neglecting contributions from more remote atoms, no serious error is introduced.

In the present paper we will consider the distribution of two kinds of atoms in a spheroidal particle, cut from a fcc crystal. This particle has no single surface plane, but exposes a considerable number of differently coordinated atoms to the vacuum and can be considered as a model catalyst particle. In contrast to calculations on thin films or slabs the number of nearest-neighbor atoms of a given atom in this particle has to be computed for each symmetrically equivalent atom. The number of missing bonds is ultimately responsible for the occurrence of segregation (*7*). In our approach we will neglect the effect of different sizes of the constituting atoms and the lattice strain (*8–10*).

THEORY

For a small catalytic bimetallic particle we consider the following model. Around a given atom we place its 12 nearest neigh-

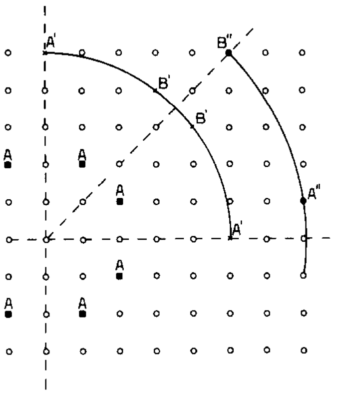

FIG. 1. Illustration of the concept of shells for a square two-dimensional lattice. All atoms A are equivalent and belong to the same shell with 8 atoms. Atoms A' and B' (and A'' and B'') are equidistant from the origin but belong to different shells, the one with B' containing 8 atoms and that with B'' 4 atoms.

bors. The first atom is denoted as shell number 1; the 12 neighbors are all equivalent and called shell number 2. Successive shells are built around the central atom in this manner, all with atoms that have the same distance to the central atom and are equivalent on symmetry grounds. The latter condition is illustrated in Fig. 1 for a two-dimensional square lattice. The atoms marked A' and B' are equidistant from the origin but nevertheless symmetrically nonequivalent. They thus belong to different shells. The total number of shells is denoted by *n*, and (in three dimensions) each shell contains 48, 24, 12, 8, 6, or 1 atoms. The numbers are a consequence of the cubic lattice generated in building the particle with a fcc structure. Each atom has neighbors in its own and other shells. They may be found by a simple computer algorithm. An example is shown in Table 1.

All calculations of the free energy of the system were performed in the Bragg–Williams approximation (*3, 11, 12*), which takes only nearest-neighbor interactions into account and computes the energy and entropy of the system for the case of random mixing. The energy of a sphere-like particle is then given by (cf. Ref. (*7*))

$$
\begin{aligned}
E = \sum_{i=1}^{n} \{ & N_i^{\mathrm{A}} \tfrac{1}{2} Z_{ii} H_{\mathrm{AA}} x_i + N_i^{\mathrm{B}} \tfrac{1}{2} Z_{ii} H_{\mathrm{BB}} (1 - x_i) \\
& + N_i^{\mathrm{A}} \tfrac{1}{2} Z_{ii} H_{\mathrm{AB}} (1 - x_i) + N_i^{\mathrm{B}} \tfrac{1}{2} Z_{ii} H_{\mathrm{AB}} x_i \} \\
& + \sum_{i=1}^{n} \Big\{ N_i^{\mathrm{A}} \sum_{j=i+1}^{n} Z_{ij} H_{\mathrm{AA}} x_j \\
& + N_i^{\mathrm{B}} \sum_{j=i+1}^{n} Z_{ij} H_{\mathrm{BB}} (1 - x_j) \\
& + N_i^{\mathrm{A}} \sum_{j=i+1}^{n} Z_{ij} H_{\mathrm{AB}} (1 - x_j) \\
& + N_i^{\mathrm{B}} \sum_{j=i+1}^{n} Z_{ij} H_{\mathrm{AB}} x_j \Big\}. \qquad (8)
\end{aligned}
$$

Here H_{kl} is the bond strength (taken as negative) between neighboring atoms *k* and *l*, N_i^{A} and N_i^{B} are the number of atoms A and B in shell *i*, Z_{ij} is the number of nearest-neighbor atoms for any atom in shell *i* with atoms in shell *j*, and x_i is the mole fraction of A in shell *i*. The first summation describes all intrashell interactions and the second double sum takes the existence of shells with $j > i$ into account. The entropy of the system is simply

$$S = k \sum_{i=1}^{n} \ln \frac{(N_i^{\mathrm{A}} + N_i^{\mathrm{B}})!}{N_i^{\mathrm{A}}! N_i^{\mathrm{B}}!}. \qquad (9)$$

Introducing the regular solution parameter Ω

$$\Omega = H_{\mathrm{AB}} - \tfrac{1}{2}(H_{\mathrm{AA}} + H_{\mathrm{BB}}) \qquad (10)$$

and the total number of atoms in a given shell N_i

TABLE 1

Description of Shells[a]

Shell	$r^2/4a^2$	N_i	Neighboring shells											
1	0	1	2	2	2	2	2	2	2	2	2	2	2	2
2	2	12	1	2	2	2	2	3	3	4	4	4	4	5
3	4	6	2	2	2	2	4	4	4	4	6	6	6	6
4	6	24	2	2	3	4	4	5	5	6	6	7	8	8
5	8	12	2	4	4	4	4	6	6	8	8	8	8	—
6	10	24	3	4	4	5	6	6	8	8	—	—	—	—
7	12	8	4	4	4	8	8	8	8	8	8	—	—	—
8	14	48	4	5	6	7	8	8	—	—	—	—	—	—

[a] Examples of the different shells, their distance and number of atoms used in the present work. Atoms in shells with numbers >8 are denoted as —. Note that only four out of eight shells are fully coordinated.

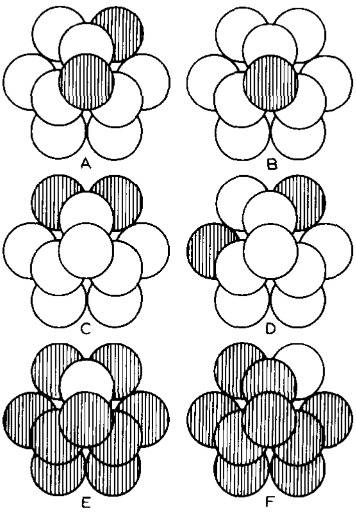

FIG. 2. Schematic drawing of an 11-atom cluster, consisting of Cu_2Ni_9 (A–D) or Ni_9Cu_2 (E–F). The clusters are made of a bottom layer of 7 atoms, followed by a middle layer of 3 and a top atom. The hatched circles represent Cu atoms. The central atom in the bottom layer is not visible in the diagram.

$$N_i = N_i^A + N_i^B \tag{11}$$

the free energy of the particle is given by

$$G = \sum_{i=1}^{n} N_i \frac{Z_{ii}}{2} \{H_{AA}x_i + H_{BB}(1 - x_i) + \Omega 2x_i(1 - x_i)\} + \sum_{i=1}^{n} N_i \sum_{j=i+1}^{n} \frac{Z_{ij}}{2} \{H_{AA}(x_i + x_j) + H_{BB}(2 - x_i - x_j) + \Omega 2(x_i + x_j - 2x_ix_j)\} + kT \ln \frac{N_i!}{(N_ix_i)!\{N_i(1 - x_i)\}!}. \tag{12}$$

The overall mole fraction $\bar{x}$ of component A is assumed to be fixed experimentally, so that the constraint

$$\bar{x} = \sum_{i=1}^{n} N_i^A \Big/ \sum_{i=1}^{n} N_i \tag{13}$$

is imposed on Eq. (12) in finding the minimum of G with respect to all x_i. Mathematically the problem is now reduced to finding the minimum value of a given function of $n - 1$ variables. Due to the smallness of the number of atoms involved ($N_i \leq 48$ for all i) we have kept the factorial in Eq. (12), and not used Stirling's approximation.

For an extremely small particle on a support a more direct approach is possible. For any specific configuration of the constituting atoms the energy may be written

$$E_j = \alpha_j H_{AA} + \beta_j H_{BB} + \gamma_j H_{AB} + \delta_j H_{AS} + \varepsilon_j H_{BS} \tag{14}$$

where the greek letters denote the number of bonds between A–A, B–B, A–B, A-support, and B-support atoms in that particular configuration. The probability of any configuration is given by Eq. (1).

For a very small particle, composed of only 9 atoms A and 2 atoms B in the structure shown in Fig. 2 there are 55 configurations and all degeneracies and number of bonds may be obtained by a simple but tedious direct count. The probabilities P_j are then directly obtained from Eq. (1). Note that this procedure gives much more information than the preceding one, since now the probability for each specific cluster of 9 A atoms and 2 B atoms is found and not just the average mole fraction of A in some shell.

RESULTS AND DISCUSSION

Calculations of the composition of each shell were made for the parameter values $H_{AA} = -13.0$ kcal/mol, $H_{BB} = -17.5$ kcal/mol, and $\Omega = 126$ cal/mol. These correspond approximately to the Cu–Ni system with A=Cu and B=Ni. Figure 3A gives the mole fraction of copper in each shell for a particle of 12 shells at two temperatures (900 and 300 K) and three average mole fractions of copper ($\bar{x} = 0.1$, 0.5, and 0.9). The particle radius is $r/a = 2.24$, or with a typical lattice constant of $a = 3.5$ Å, $r = 7.8$ Å. This particle contains 201 atoms. As expected, segregation of Cu to the surface is quite extensive. However, also in shells which contain atoms with less than 12 neighbors the amount of copper is significant. Only at the highest average mole fractions ($\bar{x} = 0.5$ and 0.9) and 300 K can a

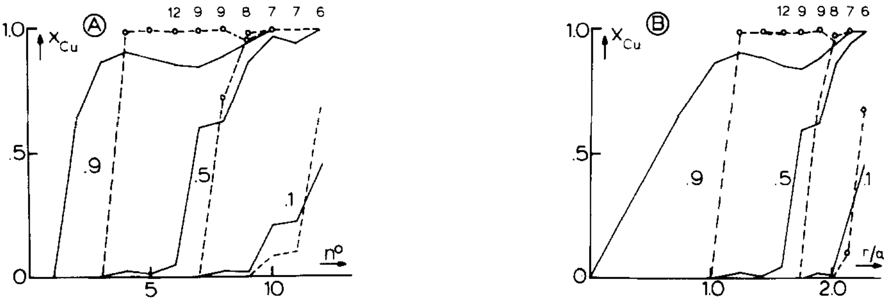

FIG. 3. Mole fraction of Cu in a spheroidal particle with 12 shells as a function of shell number (A) and distance (B) for three overall mole fractions of 0.1, 0.5, and 0.9. ---: $T = 300$ K; —: $T = 900$ K. The number of nearest neighbors is indicated for each position.

clear-cut separation between two virtually pure phases be observed. Figure 3 is nothing but an illustration of the "cherry model," proposed by Sachtler and van Santen (*4*, *13*) for alloy catalysts. Since, as has been state before, different shells may be at the same distance from the central atom, a better representation of the results is given in Fig. 3B, where the mole fraction of copper is plotted versus the reduced distance r/a.

Going to larger particles (with 32 shells, 767 atoms, and $r/a = 3.53$ or $r \simeq 12.3$ Å) much the same effects are found, as is illustrated in Fig. 4. The decrease in copper content at shell number 29 (or $r/a = 3.46$, lower drawing) is caused by the high coordination number of atoms in this shell, viz. 9, compared to 6 for the adjoining shells. This causes an oscillation of the composition profile. An inspection of the local geometry of atoms in shell number 29 shows that these atoms are the center atoms of a 7-atom (111) facet with six in-plane neighbors and three neighbors below that plane. The adjoining shells contain atoms that are part of a small four-atom (100) facet with only two in-plane neighbors.

The remarkable aspect of Figs. 3 and 4 is that a number of shells are not fully coordinated and that their constituting atoms may thus form chemical bonds with adsorbates. If we call these atoms surface atoms (although they need not be in the shell furthest removed from the center) their number is easily calculated as a function of particle size. The ratio of this number N_j to the total number of atoms in the particle is then the minimum mole fraction necessary to coat the catalytic particle completely with one component (assuming complete segregation of this component). It is then also the minimum mole fraction necessary to suppress any catalytic reaction that may require one

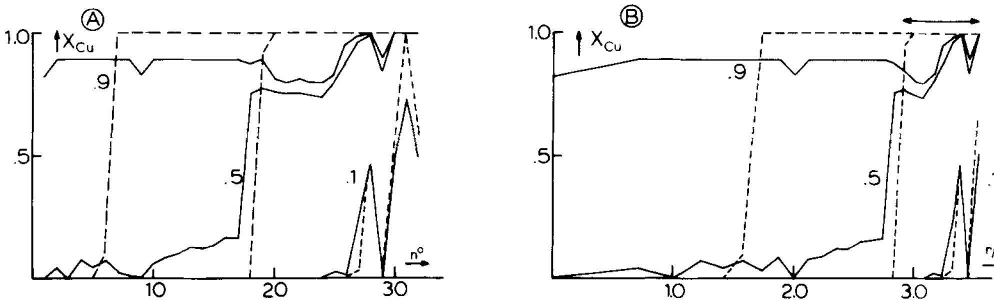

FIG. 4. As Fig. 3, except that the number of shells is now 32. The arrow denotes the region of atoms with less than 12 nearest neighbors.

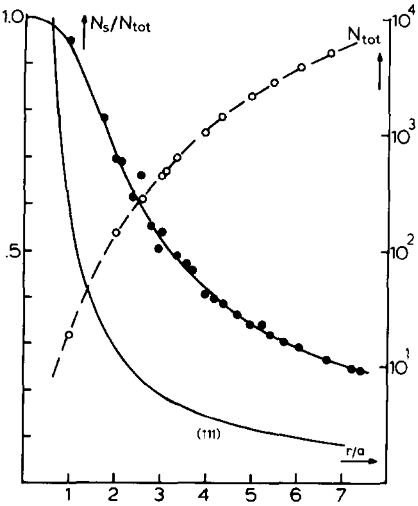

FIG. 5. The ratio of the number of surface atoms and the total number of atoms for a spheroidal particle as a function of reduced distance and the same quantity for a (111) oriented film. The total number of atoms in the particle is given on the right-hand axis.

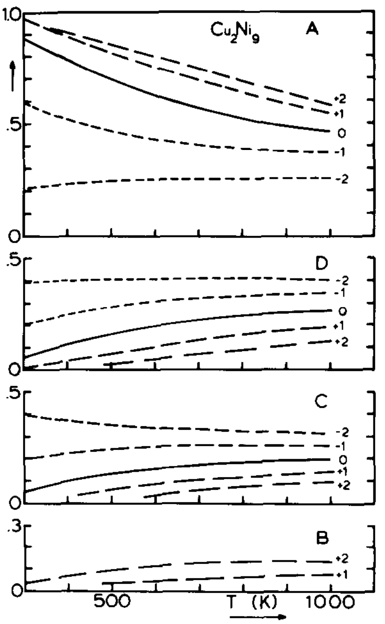

FIG. 6. The probability P of finding a specific cluster in a Cu_2Ni_9 particle as a function of temperature. The letters refer to Fig. 2 except for curves D, which also include a cluster as D, but with two copper atoms opposite each other in the bottom layer. The numbers denote the difference in bond strength with the support $\Delta = H_{Cu-S} - H_{Ni-S}$ in kcal/mole.

atom of the other component. For a film with n layers of (111) orientation the same quantity is simply $2/n$ or $\frac{1}{3}a\sqrt{3}/r$. Figure 5 shows the fraction of surface atoms in a catalytic spherical particle and a film as a function of particle radius (or half the film thickness). As can be seen, the resulting curves are quite different for the two geometries. It is thus to be expected that the catalytic properties of small particles and films with the same overall composition will be different from each other.

For very small particles, as shown in Fig. 2, a number of clusters with different atomic arrangements is possible. Figure 2 shows six clusters of 11 atoms, the top four representing Cu_2Ni_9, the bottom two Cu_9Ni_2. The probability of their occurrence as a function of temperature in accordance with statistical thermodynamics (Eq. (1)) is given in Figs. 6 and 7 as solid lines. It is evident from these drawings that more than one cluster is present at $T > 300$ K and that these clusters exhibit different catalytic sites (cf. Fig. 2). A change in temperature is accompanied by a change in cluster distribution and thus a possible trivial change in catalytic performance.

The effect of bonding to the support can also be discussed for these clusters. In the solid curves the assumption has been made that both components bind equally well to

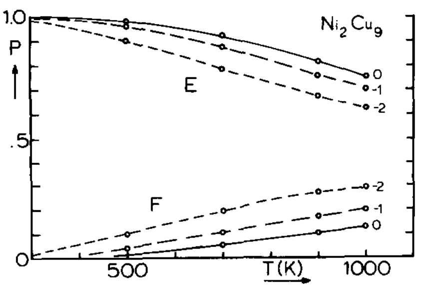

FIG. 7. Probability P of finding a specific cluster in a Ni_2Cu_9 particle as a function of temperature. The letters refer to the clusters shown in Fig. 2. The numbers denote the difference in bond strength with the support $\Delta = H_{Ni-S} - N_{Cu-S}$ in kcal/mole. Curves for $\Delta = +1$ and $+2$ are almost identical to the ones with $\Delta = 0$.

the support, i.e., $\Delta \equiv H_{AS} - H_{BS} = 0$. Changing the relative bond strengths by ±1 or ±2 kcal/mole produces the dashed curves in Figs. 6 and 7. The effect is seen to be appreciable for all clusters, some decreasing in abundance, others increasing. Again, in all cases more than one cluster is present, which will influence the catalytic behavior of the particles. Although we have demonstrated the effect for very small particles, the same results are expected for larger clusters, which are unfortunately difficult to model in the same way.

In concluding we may state that, due to particle surface topography, a small catalytic particle has significantly more surface atoms exposed to a gas phase than a flat film. The precise structure of the outer layers of the particle may lead to oscillations in the composition profile. The suppression of catalytic activity by segregation of one component requires a lower mole fraction for films than for spheroidal particles. Identical particles (in terms of overall composition) can still occur as chemically distinguishable clusters, with different catalytic properties. Small differences in bond strength to the support may alter the cluster distribution at a given temperature. A change in temperature will also produce a different cluster distribution with a concomitant change in catalytic performance.

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