

Theory of Surface Enrichment in Disordered Monophasic Binary Alloys. Numerical Computations for Ag-Au Alloys

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The regular solution model is used to compute the surface enrichment in the (111)- and (100)-faces of silver-gold alloys. Surface enrichment by silver is predicted to increase if the surface plane becomes less saturated and decreases if one raises the temperature. The possible implications of these findings are considered in the light of the recently reported mechanism of the epoxidation of ethylene over silver catalysts.

I. INTRODUCTION

Studies of the catalytic behavior of alloys have shown that their selectivity is not simply determined by the "sum" of the catalytic properties of their constituents (1, 2). To explain this phenomenon we need some information about the composition of the actual surface exposed to the reacting molecules, because there is experimental evidence that one of the factors causing the deviation from additivity is a difference between surface and bulk compositions (3, 4). Only after this difference has been accounted for can one hope to distinguish the geometric effects from the electronic ones.

A quantitative study of surface enrichment has been made possible by recent developments in the use of Auger spectroscopy. By employing an internal standard (5) many of the ambiguities of previous applications are removed, but as several outer layers are sampled one should still be careful in interpreting the

data and compare them not only with those obtained from other experiments such as chemisorptive titration (6, 7) but also with theory.

Surface enrichment in biphasic alloys, such as copper-nickel, has been extensively discussed and satisfactorily explained by Sachtler *et al.* (3, 4, 8) who introduced the cherry model. Monophasic alloys can be subdivided into ordered alloys, often called compounds, and disordered alloys. A previous investigation of ours concerned the surface enrichment in an alloy of the former type (9). Here we will concentrate on a disordered alloy, which forms a continuous series of solid solutions.

An early approach to the problem was considered by Ollis (10); he paid special attention to the crystallographic face dependence of surface enrichment. Fortunately, there is a rich literature on the surface tension and enrichment of liquids (11, 12) and although a solid and a liquid are widely different, some of the statistical mechanical theories used to compute surface enrichment in liquid binary solutions treat the liquid as if it were a crystal of hard spheres.

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Within the regular solution model, Defay *et al.* (11) and Guggenheim (13) have given the following formula:

$$kT \ln \left(\frac{y}{1-y} \right) \left(\frac{x}{1-x} \right)^{-1} + \frac{m}{4} (\epsilon_2 - \epsilon_1) + \alpha \left\{ (2l + m)x - 2ly - \frac{m}{2} \right\} = 0, \quad (1)$$

where

x, y	concentrations of component 1 in bulk and surface, respectively (at %),
ϵ_1, ϵ_2	bond energies between nearest neighbor spheres of component 1 and component 2, respectively,
α	$\epsilon_{12} - \frac{1}{2}(\epsilon_1 + \epsilon_2)$,
ϵ_{12}	bond energy between nearest neighbor spheres of component 1 and 2,
l	number of nearest neighbor bonds per atom in plane parallel to surface plane,
m	number of nearest neighbor bonds per atom in bulk outside plane parallel to surface plane.

All unsaturated atoms are thought to be arranged in one plane. Only nearest neighbor interactions are taken into account in the derivation of Eq. (1). A second assumption made is that only in the outer layer is there a difference in composition with the bulk.

Defay and Prigogine (14) pointed out that only if one takes into account changes in the two outer layers Gibbs rule, the exact thermodynamic law that determines surface enrichment, can be satisfied. So, at least the two outer layers have to be considered. We have shown previously (9) that this is certainly the case in an ordered alloy. As long as the temperature is high compared with the critical temperature of demixing or ordering, the deviations in any layer other than the outer layer are very small (12, 14). Of course, if short range order is important, which is the case near the critical temperature, concentration changes in more than only the outer layer would occur (9). If alloying is endothermic ($\alpha > 0$) this implies also enrichment in the second layer. However, if alloying is

an exothermic process ($\alpha < 0$) depletion in the second layer by the component which enriches in the surface layer would occur.

The first term in Eq. (1) is due to the difference in entropy between the surface layer and the bulk. The decrease in entropy on enrichment is balanced by the gain in enthalpy, determined by the different number of bonds broken in the surface and bulk on enrichment. In the Appendix Eq. (1) will be derived for the (111)-face of a face-centered cubic crystal. It appears that as long as α is small enrichment will only occur in the component with the smallest bond energy.

II. NUMERICAL COMPUTATIONS FOR SILVER-GOLD ALLOYS

To apply Eq. (1) to an actual alloy, one has to derive the bond energies and α from experimental values. If Ω denotes the heat of formation of the alloy, α can be determined from

$$\alpha = \frac{1}{l + m} \Omega. \quad (2)$$

The bond energies ϵ_1 and ϵ_2 can be derived from the sublimation energies of the metal by:

$$\epsilon_1 = \frac{2E_{\text{subl}}}{l + m} \quad (3)$$

or from the surface energies σ by:

$$\epsilon_1 = -\frac{4a_1\sigma_1}{m}, \quad (4)$$

where a_1 = surface area of atom 1.

If one uses formula (3) to compute ϵ and substitutes this value in Eq. (4) to compute σ , one finds for silver [heat of sublimation 274.2 kJ/g at (15)] and gold [heat of sublimation 378.3 kJ/g at, (15)]:

$$\sigma_{\text{Ag}(111)} = 1.6, \sigma_{\text{Ag}(100)} = 1.8, \sigma_{\text{Au}(111)} = 2.2, \\ \sigma_{\text{Au}(100)} = 2.5 \text{ J/m}^2.$$

The experimental values at the melting point are (16):

$$\sigma_{\text{Ag}} = 0.9, \sigma_{\text{Au}} = 1.2 \text{ J/m}^2.$$

The difference between experimental and

theoretical values is too large to be explained by the fact that the experimental points have been measured near the melting points and that the theory applies to solids. This difference is usually a factor 4/3 (17). We ascribed this difference to the energy released by electrons which adjust their movement to the surface. If electrons are completely delocalized, a LCAO model with 1 electron per atomic orbital gives a decrease in surface energy by a factor $\frac{1}{2}$ compared with the value found from the hard sphere model (18). For this reason we have used Eq. (4) to compute the bond energies.

The final formula to solve is:

$$kT \ln \left(\frac{y}{1-y} \right) \left(\frac{x}{1-x} \right)^{-1} + \frac{m}{m'} (a'_1 \sigma'_1 - a'_2 \sigma'_2) + \frac{\Omega}{l+m} \left\{ (2l+m)x - 2ly - \frac{m}{2} \right\} = 0, \quad (5)$$

where $\frac{1}{4} m' =$ number of bonds that has to be broken to form one surface atom in a plane with surface energy σ' . The value of Ω in the Ag-Au alloy is -6.65 kJ/g at. In the computations we have chosen the surface energy σ' to belong to the (111)-plane, the most density packed plane in a fcc crystal, which structure silver and gold possess. So, m' amounts to 6.

Neglecting the difference between a'_1 and a'_2 reduces Eq. (5) to:

$$kT \ln \left(\frac{y}{1-y} \right) \left(\frac{x}{1-x} \right)^{-1} + \frac{am}{6} \Delta\sigma + \frac{\Omega}{l+m} \left\{ (2l+m)x - 2ly - \frac{m}{2} \right\} = 0, \quad (6)$$

where $a =$ average area of atoms 1 and 2 in the (111)-face.

The results of the calculations, which were carried out for 250 and 500°C, are plotted in Figs. 1 and 2 for the (111)- and (100)-planes, respectively. Within this temperature region the Ag-Au alloys form a continuous series of solid solutions.

As expected, we find a decrease in gold

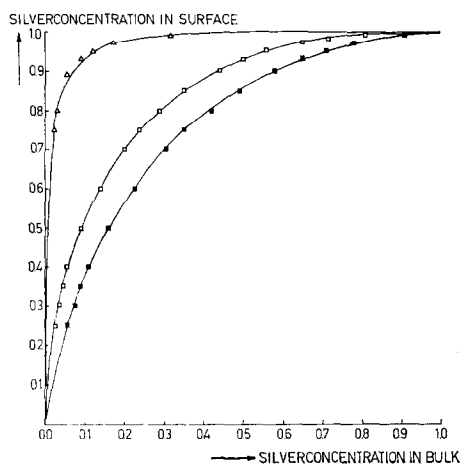


FIG. 1. Surface enrichment ($\Delta\sigma$) in the (111)-plane of silver-gold alloys: (□) 0.3 J/m², 250°C; (■) 0.3 J/m², 500°C; (△) 0.6 J/m², 250°C.

concentration, viz, surface enrichment by silver. The surface enrichment is more pronounced in the (100)- than in the (111)-plane. This is not surprising, because the number of bonds broken to form the (100)-surface is larger than that required to form the (111)-surface. A temperature increase from 250 to 500°C diminishes the extent of surface enrichment by silver.

To illustrate the effect of the difference between the calculated and experimental

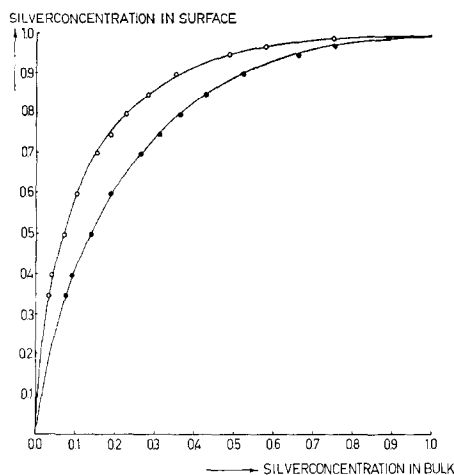


FIG. 2. Surface enrichment ($\Delta\sigma$) in the (100)-plane of silver-gold alloys: (○) 0.3 J/m², 250°C; (●) 0.3 J/m², 500°C.

surface energy values upon surface enrichment the calculations for the (111)-plane at 250°C were carried out with both values. As can be seen from Fig. 1, a difference in surface energy of 0.3 J/m² has a rather large effect upon surface enrichment in these alloys.

No experimental data on surface enrichment in the silver-gold system are known. However, experimental data on changes in the work function of silver-palladium alloys are available (19). This system also forms a solid solution, and the difference in surface energy between palladium and gold is very small. The experimental curves show a very similar behavior to our curves computed with the experimental difference in surface energy.

II. CATALYTIC IMPLICATIONS

Both in the heterogeneous gas-phase oxidation of ethylene to ethylene oxide and in the oxidation of liquid cumene hydroperoxide, silver-gold alloys are known to display a higher selectivity than pure silver catalysts (20, 21). If it is assumed that gold has the same effect upon selectivity as the chlorine compounds usually added to the feed in an industrial ethylene oxide process, then its positive effect can be attributed to the formation of diatomic chemisorbed oxygen ions (O₂⁻) being preferred to that of dissociatively adsorbed oxygen species. The question arises whether this is exclusively due to the particular geometry of the "ensembles" of adsorbing atoms, as seems to be the case with the chlorine modifier (22). If so, we would expect the optimum yield at a surface composition of about 25% gold-75% silver, since the necessary steady state coverage of the silver surface (containing 12×10^{18} silver atoms m⁻²) by chlorine is 3×10^{18} chlorine atoms m⁻² (20). In view of this it is striking that according to our calculations even at a gold concentration in the bulk of 70% only 10-20% gold will appear in either surface at 250°C. In other words, if the preferred formation of the O₂⁻ ions were exclusively due to a geometric "ensemble" effect, the dilution of silver-

gold alloys necessary for a high selectivity to ethylene oxide would only be attainable at very high gold concentrations in the bulk. As this is in contrast with the observations of Flank and Beachell (20) and Van Ham, Nieuwenhuis and Sachtler (21), it would seem that the positive influence of gold on the selectivity of ethylene oxidation is due to several factors rather than purely to a geometric effect. In addition, changes in the surface composition from the equilibrium will also occur as a result of the surrounding ethylene/oxygen atmosphere. Conclusive information about which of these effects plays a major role in ethylene oxidation will be obtained by measuring surface composition by means of Auger spectroscopy and/or chemisorptive titration.

APPENDIX. DERIVATION OF EQUATION (1) FOR A (111)-FACE OF A FCC CRYSTAL

Let us assume N atoms to be present in the bulk and N' atoms in the surface monolayer. Then for large particles $N' \ll N$. If the compositions of surface monolayer and bulk are the same, the entropy of mixing of the system is given by:

$$-k(N + N')[(1 - x) \ln(1 - x) + x \ln x], \quad (\text{A1})$$

x being the atomic fraction of component 1. If this component is enriched in the surface by a fraction Δ , the entropy of the surface becomes:

$$-kN'[(1 - x - \Delta) \ln(1 - x - \Delta) + (x + \Delta) \ln(x + \Delta)] \quad (\text{A2})$$

and that of the bulk:

$$-kN[(1 - x + \Delta') \ln(1 - x + \Delta') + (x - \Delta') \ln(x - \Delta')]. \quad (\text{A3})$$

The number of particles has to be conserved, thus,

$$\Delta' = \frac{N'}{N} \Delta. \quad (\text{A4})$$

The sum of Eqs. (A2) and (A3) less Eq. (A1) gives the change in entropy $S(\Delta)$:

$$S(\Delta) = kN' \left[(1-x) \ln(1-x) + x \ln x + \Delta \ln \frac{x}{1-x} - (1-x-\Delta) \ln(1-x-\Delta) - (x+\Delta) \ln(x+\Delta) \right]. \quad (\text{A5})$$

We shall later require the derivative:

$$\frac{\partial S(\Delta)}{\partial \Delta} = kN' \ln \left\{ \frac{x(1-x-\Delta)}{(1-x)(x+\Delta)} \right\}. \quad (\text{A6})$$

Having derived the change in entropy, we shall now proceed to calculate the change in enthalpy. We give the derivation for the (111)-face of a fcc crystal.

The energy of one atom of component 1 in the bulk is:

$$E^b(1) = 12\{x\epsilon_1 + (1-x)\epsilon_{12}\}. \quad (\text{A7a})$$

The energy of this atom at the surface is:

$$E^s(1) = 6\{(x+\Delta)\epsilon_1 + (1-x-\Delta)\epsilon_{12} + 3\{x\epsilon_1 + (1-x)\epsilon_{12}\}\}. \quad (\text{A7b})$$

The expressions for component (2) are:

$$E^b(2) = 12\{x\epsilon_{12} + (1-x)\epsilon_2\}, \quad (\text{A8a})$$

$$E^s(2) = 6\{(x+\Delta)\epsilon_{12} + (1-x-\Delta)\epsilon_2 + 3\{x\epsilon_{12} + (1-x)\epsilon_2\}\}. \quad (\text{A8b})$$

The change in enthalpy on surface enrichment is given by:

$$E(\Delta) = N' \int_0^\Delta d(\Delta') \{E^s(1) + E^b(2) - E^s(2) - E^b(1)\}. \quad (\text{A9})$$

The results for $E(\Delta)$ is:

$$E(\Delta) = N'\Delta \left\{ 2\alpha(3x - 3\Delta) - 3\alpha + \frac{3}{2}(\epsilon_2 - \epsilon_1) \right\}, \quad (\text{A10})$$

with

$$\alpha = \epsilon_{12} - \frac{1}{2}(\epsilon_1 + \epsilon_2).$$

We must now compute the value of Δ for which the change in free energy reaches a minimum. The first derivative of $E(\Delta)$ is given by:

$$\frac{\partial}{\partial \Delta} E(\Delta) = N' \left\{ 2\alpha(3x - 6\Delta) - 3\alpha + \frac{3}{2}(\epsilon_2 - \epsilon_1) \right\}. \quad (\text{A11})$$

From the condition:

$$\frac{\partial}{\partial \Delta} E(\Delta) = T \frac{\partial S(\Delta)}{\partial \Delta} \quad (\text{A12})$$

one finds as expression for Δ :

$$3\alpha(2x - 4\Delta - 1) + \frac{3}{2}(\epsilon_2 - \epsilon_1) - kT \ln \frac{x(1-x-\Delta)}{(1-x)(x+\Delta)} = 0, \quad (\text{A13})$$

substituting

$$y = x + \Delta \quad (\text{A14})$$

(A13) becomes:

$$kT \ln \left(\frac{y}{1-y} \right) \left(\frac{x}{1-x} \right)^{-1} + \frac{3}{2}(\epsilon_2 - \epsilon_1) + 12\alpha \left\{ \frac{1}{2}(1-2y) - \frac{3}{4}(1-2x) \right\} = 0 \quad (\text{A15})$$

(A15) equals Eq. (1) if one sets $l = 6$, $m = 6$.

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