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THE REGULAR SOLUTION THEORY

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THE SURFACE COMPOSITION OF BINARY METAL ALLOYS.
THE REGULAR SOLUTION THEORY

A. Jabłoński*
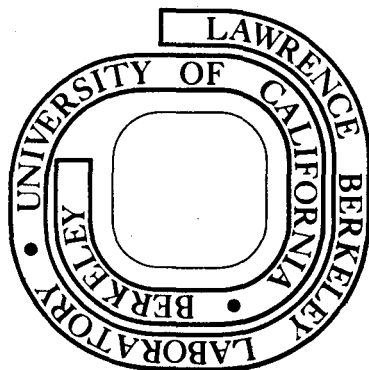
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ABSTRACT

A theory predicting the surface composition of binary metal alloys on the basis of thermodynamic data has been presented. The equation describing the surface composition has been derived for the random solution model and the short range order model. The surface compositions calculated for both models were found not to differ significantly. The experimentally determined surface compositions of binary metal alloys by means of the Auger electron spectroscopy were reviewed and compared with the presented theory. The theory was found to predict the direction of surface enrichment, but the extent of surface segregation was overestimated in most of the cases.

A.   INTRODUCTION

In recent years several experimental studies were published indicating that the surface composition of metal alloys differs from bulk composition.[1-14] Simple theoretical models were developed on the basis of the theory of regular solutions to account for this phenomenon.[15-17] In the present paper the theory will be generalized and a more advanced model will be introduced.

The term "regular solution" was introduced by Hildebrand in 1929.[18] The regular solutions were defined as solutions of a common solute in various solvents having the same entropy of mixing as ideal solutions of the same mole fraction.   The theory presented in this paper is based on definition due to Guggenheim and Fowler.[19] It concerns more restricted classes of mixtures, called by those authors "strictly regular solutions".   Those solutions have the following properties:

1.   Any atom of the solution has the same number of first nearest neighbors in the whole range of concentrations.

2.   The ratio of molecular volumes of constituents ranges from 1 to 2, or the ratio of the diameters of atoms is between 1 and 1.26.

3.   The ratio of the free volumes of pure components does not differ from unity by more than 30%.

4.   After mixing two constituents in a constant temperature and pressure the molecular volumes as well as free volumes remain unaltered.

5.   The potential energy of the mixture is the sum of the potential energies of the pairs of closest neighbors.

The mathematical approach allowing the determination of bulk properties of such defined solutions was developed by Guggenheim.[20] This approach will be applied to describe the surface properties of binary metal alloys.

B.   THEORY

In this section we will derive the general equation describing the composition of surface layer in the binary metal alloy on the basis of a

strictly regular solution model. Let us consider a solution of two

metals A and B, and let us denote:

N_A — the number of A atoms in the alloy,

N_B — the number of B atoms in the alloy,

N — the total number of atoms in the alloy,

N_{AA} — the number of A-A bonds;

N_{BB} — the number of B-B bonds,

N_{AB} — the number of A-B bonds,

H_{AA} — the energy of A-A bond,

H_{BB} — the energy of B-B bond,

H_{AB} — the energy of A-B bond,

x_A, x_B —the atom fractions of constituents A and B, respectively.

For convenience we will choose the dissociated atom pairs in gaseous state

as standard state. Thus, the energy H_{AA} of forming of A-A bond is associated

with the reaction

$$A_{(g)} + A_{(g)} = A - A_{(s)} .$$
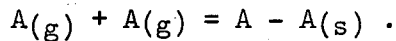
Let the system under consideration consist of the surface region one atom

thick being in equilibrium with the bulk of the alloy. Then the following

equation holds

$$\partial F/\partial x_A^S = \partial U/\partial x_A^S - T\partial S/\partial x_A^S = 0 , \tag{1}$$

where F, U, S are the usual notations for thermodynamical functions, i.e.

the total free energy, the total energy and the total entropy of the system,

respectively; x_A^S is the atom fraction of component A in the surface layer.

Let us carry out the process resulting in surface enrichment in component A.

1. Remove one B atom from the surface layer to infinity.

2. Remove one A atom from the bulk of the alloy to infinity.

3. Place the A atom on the surface.

4. Place the B atom in the bulk of the alloy.

It will be necessary to know for further considerations, the probability, P_B, that a given neighbor of atom B is atom A. On the average, there are N_{AB}/N_B bonds A-B per one atom B. Since the total number of neighbors of any atom is equal to Z, we have $P_B = N_{AB}/ZN_B$. It is also necessary to know the probability, P_A, that a given neighbor of atom A is atom B. The same argument gives $P_A = N_{AB}/ZN_A$. The probabilities P_A and P_B are the functions of composition of the alloy.

Now we can express the energies of particular stages of the considered process.

$$\Delta U_1 = -Z_p[1 - P_B(x_A^s)]H_{BB} - Z_p P_B(x_A^s)H_{AB}$$
$$- Z_v[1 - P_B(x_A)]H_{BB} - Z_v P_B(x_A)H_{AB},$$

$$\Delta U_2 = -ZP_A(x_A)H_{AB} - Z[1 - P_A(x_A)]H_{AA},$$

$$\Delta U_3 = Z_p[1 - P_A(x_A^s)]H_{AA} + Z_p P_A(x_A^s)H_{AB}$$
$$+ Z_v[1 - P_A(x_A)]H_{AA} + Z_v P_A(x_A)H_{AB},$$

$$\Delta U_4 = Z[1 - P_B(x_A)]H_{BB} + ZP_B(x_A)H_{AB}.$$

Here Z_p is the number of first nearest neighbors in the lateral direction, in the plane containing the atom, and Z_v is the number of first nearest neighbors in the vertical direction, to the one side of the plane containing the atom: $Z = Z_p + 2Z_v$. The energy of the total considered process is equal to the sum of particular stages, $\Delta U = \sum_1 \Delta U_i$. For the sake of simplified notation we will introduce into the resulting formula the regular solution parameter Ω defined as

$$\Omega = H_{AB} - \tfrac{1}{2}(H_{AA} + H_{BB}), \tag{2}$$

and the short range order parameter, α_1, defined as[21]

$$\alpha_1 = 1 - P_B/x_A = 1 - P_A/x_B = 1 - N_{AB}/ZNx_A x_B. \tag{3}$$

The molar heats of sublimation of pure components can be expressed as

$H_A^{sub} = -\frac{1}{2}ZN_O H_{AA}$ and $H_B^{sub} = -\frac{1}{2}ZN_O H_{BB}$, where N_O is the Avogadro number. We have then

$$H_{AA} = -2H_A^{sub}/ZN_O \ ,$$
$$H_{BB} = -2H_B^{sub}/ZN_O \ . \tag{4}$$

Introducing (2)-(4) into expression for ΔU we obtain

$$\Delta U = \Omega Z\{\ell[1-\alpha_1(x_A^S)](1-2x_A^S) - (\ell+m)[1-\alpha_1(x_A)](1-2x_A)\}$$
$$+ [m-\ell\alpha_1(x_A^S) + (\ell+m)\alpha_1(x_A)](H_A^{sub}-H_B^{sub})/N_O \tag{5}$$

where $\ell = Z_p/Z$ and $m = Z_v/Z$. Moving one A atom to the surface results in a concentration increase of component A equal to $\Delta x_A^S = 1/N^S$, where N^S is the total number of atoms in the surface layer. The ratio

$$\Delta U/\Delta x_A^S = N^S \Delta U \tag{6}$$

can be considered as the approximate value of the derivative $\partial U/\partial x_A^S$.

Let us evaluate now the derivative $\partial S/\partial x_A^S$. An increase of concentration of component A on the surface results in decreasing concentration of A in the bulk, so $N^S dx_A^S = -Ndx_A$. The total entropy of the system,S, is the sum of the entropy of the bulk, S^b, and the entropy of the surface layer, S^S. Therefore

$$\partial S/\partial x_A^S = \partial S^S/\partial x_A^S + \partial S^b/\partial x_A^S$$
$$= (N^S/N_O)(\partial s^S/\partial x_A^S - \partial s^b/\partial x_A), \tag{7}$$

where s^S and s^b are molar entropies of surface layer and of bulk, respectively. Those values can be determined from relations

$$s^S = x_A^S s_A^\cdot + x_B^S s_B^\cdot + \Delta s_m^S \ ,$$
$$s^b = x_A s_A^\cdot + x_B s_B^\cdot + \Delta s_m \ ,$$

where Δs_m^S and Δs_m are molar entropies of mixing in the surface layer and in bulk, respectively, $s_A^\cdot$ and $s_B^\cdot$ are molar entropies of pure components A and B. After substituting those relations into (7) we obtain

$$\partial S/\partial x_A^S = (N^S/N_O)(\partial \Delta s_m^S/\partial x_A^S - \partial \Delta s_m/\partial x_A).$$

Let us assume that Δs_m is given by the same function of concentration in the bulk and in the surface layer, and let us denote $\partial \Delta s_m / x_A = W(x_A)$. We obtain then

$$\partial S/\partial x_A^S = (N^S/N_O)[W(x_A^S) - W(x_A)]. \tag{8}$$

Eventually, substituting (5), (6) and (8) into (1) leads to the equation

$$\Omega Z N_O \{\ell[1-\alpha_1(x_A^S)](1-2x_A^S) - (\ell+m)[1-\alpha_1(x_A)](1-2x_A)\}$$

$$+ [m-\ell\alpha_1(x_A^S) + (\ell+m)\alpha_1(x_A)](H_A^{sub}-H_B^{sub}) \tag{9}$$

$$- T[W(x_A^S) - W(x_A)] = 0.$$

In order to solve this equation, i.e. determine the surface concentration x_A^S for an alloy having bulk concentration x_A, it is necessary to know the concentration dependence of short range order parameter α_1, the concentration dependence of molar entropy of mixing, the parameter Ω, and the molar heats of sublimation of pure components. The functions $\alpha_1(x_A)$ and $W(x_A)$ as well as parameter Ω can be evaluated using the methods of statistical thermodynamics. To simplify our considerations we will derive only configurational thermodynamical functions. At the beginning we will estimate the configurational partition function for an alloy. It is given by the formula

$$Q_c = \sum_i g_i \exp(-E_i/kT) ,$$

where g_i is the number of different configurations having the same energy E_i, k is the Boltzmann constant. The energy of formation of the alloy from the dissociated gas is given by

$$U = N_{AA}H_{AA} + N_{BB}H_{BB} + N_{AB}H_{AB}$$

$$= \tfrac{1}{2}ZN_A H_{AA} + \tfrac{1}{2}ZN_B H_{BB} + \Omega N_{AB} .$$

Then the configurational partition function becomes

$$Q_c = \sum_{N_{AB}} g(N_A, N_B, N_{AB}) \exp[-\tfrac{1}{2}Z(N_A H_{AA}+N_B H_{BB}+2\Omega N_{AB}/Z)/kT], \tag{10}$$

where the sum is extended over all values of N_{AB}. The main problem consists in determining the function $g(N_A, N_B, N_{AB})$. Usually certain simplifying assumptions are introduced. We will consider two cases: the case of a random solution and the case of a solution with short range order.

(i) The random solution

Let us consider any place in the lattice of the alloy. In the case of random solution, atom A can be found in this place with probability x_A, and atom B with probability x_B. The probability that any randomly chosen pair of neighbors consists of two different atoms, A and B, is equal then to $2x_A x_B$. Hence the total number of A-B bonds is given by

$$N_{AB} = ZN x_A x_B \ . \tag{11}$$

In order to evaluate the partition function it is assumed that N_{AB} has only one value, given by the above formula, and the corresponding number of configurations, g, is equal to the total number of configurations, $N!/N_A!N_B!$. Applying the Stirling formula, $\ln N! \cong N \ln N - N$ we obtain from (10)

$$
\begin{aligned}
\ln Q_c \cong\ & -N(x_A \ln x_A + x_B \ln x_B) \\
& - \tfrac{1}{2} ZN(x_A H_{AA} + x_B H_{BB} + 2\Omega x_A x_B)/kT.
\end{aligned} \tag{12}
$$

The molar entropy of mixing can be determined from the following formulas and definitions:

$$\Delta U_m = U - \tfrac{1}{2} ZN_A H_{AA} - \tfrac{1}{2} ZN_B H_{BB} = \Omega N_{AB} \ , \tag{13}$$

where ΔU_m is the energy of mixing;

$$F_c = -kT \ln Q_c, \tag{14}$$

where F_c is the configurational free energy;

$$\Delta F_m = F_c - \tfrac{1}{2} ZN_A H_{AA} - \tfrac{1}{2} ZN_B H_{BB} \ , \tag{15}$$

where ΔF_m is the configurational free energy of mixing;

$$\Delta s_m = (N_O/N)(\Delta U_m - \Delta F_m)/T \ . \tag{16}$$

These formulas, together with equations (11) and (12), lead to the expression

$$\Delta s_m = -R(x_A \ln x_A + x_B \ln x_B) \, ,$$

where $R = kN_O$ is the gas constant. This is the molar entropy of mixing in the case of ideal solution, so random solution is also a regular solution in a sense of definition by Hildebrand.

The Ω parameter can be estimated from experimentally determined values of heat of mixing or values of activity coefficients. The dependence of heat of mixing on the Ω parameter is given by formula (13). The activity coefficients can be obtained by differentiating the function F_c with respect to N_A or N_B

$$(\partial F_c/\partial N_A)_{N_B=\text{const}} = \mu_A = \tfrac{1}{2}ZH_{AA} + kT \ln x_A + \Omega Z x_B^2 \, ,$$
$$(\partial F_c/\partial N_B)_{N_A=\text{const}} = \mu_B = \tfrac{1}{2}ZH_{BB} + kT \ln x_B + \Omega Z x_A^2 \, ,$$

where μ_A, μ_B are the chemical potentials of components A and B, respectively. Comparing the above with the following equations

$$\begin{aligned} \mu_A - \mu_{oA} &= kT \ln \gamma_A x_A \\ \mu_B - \mu_{oB} &= kT \ln \gamma_B x_B \end{aligned} \qquad (17)$$

we obtain immediately

$$\begin{aligned} \ln \gamma_A &= \Omega Z x_B^2/kT \, , \\ \ln \gamma_B &= \Omega Z x_A^2/kT \, . \end{aligned} \qquad (18)$$

(ii) The short range order solution

The case of random solution is a crude approximation of the real solution. We can expect that the value of N_{AB} is equal to that given by formula (11) when the energies of bonds A-A, B-B and A-B are close to each other and $\Omega = 0$, i.e. in the case of ideal solution. If H_{AB} is greater than both H_{AA} and H_{BB},

one can expect that the atom A would prefer atom B as a neighbor.   In alloy

then there will be more A-B bonds than in random solution.   The Ω value is then

negative (the formation of bond A-B is exothermic reaction, so H_{AB} is negative).

When H_{AB} is smaller than H_{AA} and H_{BB}, the reverse is true.   Guggenheim[20]

evaluated the function N_{AB} and the thermodynamic functions taking into

account the possibility of the short range order in cases when $\Omega \neq 0$.   Since

this approach was supposed to describe the real alloy more precisely than

random solution model, it was called "the first approximation" by Guggenheim.

This author derived the following formula, giving the number of configurations

of atoms in an alloy

$$g(N_A,N_B,N_{AB}) = \frac{(N_A+N_B)!}{N_A!N_B!} \frac{[\frac{1}{2}(ZN_A-Y)]! (\frac{1}{2}Y)! (\frac{1}{2}Y)! [\frac{1}{2}(ZN_B-Y)]!}{[\frac{1}{2}(ZN_A-N_{AB})]!(\frac{1}{2}N_{AB})!(\frac{1}{2}N_{AB})![\frac{1}{2}(ZN_B-N_{AB})]!} \quad (19)$$

where $Y = ZN_AN_B/(N_A+N_B) = N_{AB}^{random}$.   The configurational partition function is

obtained by introducing expression (19) into (10).   To simplify the resulting

formula Guggenheim proposed to replace the sum in function (10) by its maximum

term.   This term can be determined by choosing a value of N_{AB}, giving the

maximum value of function under the sign of sum.   Differentiating the logarithm

of this function with respect to N_{AB} and equating it to zero leads eventually

to the equation

$$N_{AB}^2 = (ZN_A-N_{AB})(ZN_B-N_{AB}) \exp(-2\Omega/kT) .$$

The solution has the form

$$N_{AB} = ZNx_Ax_B \frac{2}{\beta+1} \quad (20)$$

where $\beta = [1+4x_Ax_B(\exp(2\Omega/kT) - 1)]^{\frac{1}{2}}$.   The configuration partition function

is then given by

$$\ln Q_C \;\tilde{=}\; \ln g(N_A, N_B, N_{AB}) - \tfrac{1}{2}Z(N_A H_{AA} + N_B H_{BB} + 2\Omega N_{AB}/Z)/kT$$

$$
\begin{aligned}
= \; & -N(x_A \ln x_A + x_B \ln x_B) \\
& -\tfrac{1}{2}ZN\left[x_A \ln \frac{\beta+1-2x_B}{x_A(\beta+1)} + x_B \ln \frac{\beta+1-2x_A}{x_B(\beta+1)} \right] \\
& -\tfrac{1}{2}ZN_A H_{AA}/kT - \tfrac{1}{2}ZN_B H_{BB}/kT.
\end{aligned}
\tag{21}
$$

In the same way as in the case of random solution, i.e. employing formulas (13)-(16) together with functions (20) and (21) we obtain the molar entropy of mixing

$$
\begin{aligned}
\Delta s_m = \; & -R(x_A \ln x_A + x_B \ln x_B) \\
& -\tfrac{1}{2}ZR\left[x_A \ln \frac{\beta+1-2x_B}{x_A(\beta+1)} + x_B \ln \frac{\beta+1-2x_A}{x_B(\beta+1)} \right] \\
& + 2N_O Z x_A x_B \Omega/(\beta+1)T \quad .
\end{aligned}
\tag{22}
$$

Also, the coefficients of activity can be obtained in the same way as previously, i.e. by differentiating the function $F_C = -kT \ln Q_C$ with respect to N_A or N_B and comparing with formulas (17). These coefficients are given by

$$
\gamma_A = \left(\frac{\beta+1-2x_B}{x_A(\beta+1)} \right)^{\tfrac{1}{2}Z}, \qquad
\gamma_B = \left(\frac{\beta+1-2x_A}{x_B(\beta+1)} \right)^{\tfrac{1}{2}Z}
\tag{23}
$$

Knowing the expressions for N_{AB} and Δs_m we can determine the functions necessary for solving the equation (9), i.e. functions $\alpha_1(x_A)$ and $W(x_A)$. Table I lists the resulting functions for random solution and for short range order solution. Parameter Ω can be calculated from values of activity coefficients by means of formulas (18) or (23), or from heat of mixing by means of formula (13). The respective expressions are also shown in Table I. The thermodynamic data, i.e. the coefficients of activity, the heats of mixing and the heats of sublimation of pure components are extensively tabulated by Hultgren et al.[22,23]

Guggenheim[20] also derived the higher approximations of thermodynamic functions for regular solutions, considering triplets and quadruplets of atoms instead of pairs. The resulting formulas were very complicated. Comparison of thermodynamic functions calculated on the basis of random

solution model and on the basis of first, second and third approximations showed that the higher approximations differ only slightly from the first one.   The difference was more pronounced between random solution and the first approximation.

It was proven that the heat of sublimation of metals is directly proportional to their molar surface energy, i.e. to the product of surface tension and molar surface area.[17] The difference of heats of sublimation can be replaced then by the difference of respective surface energies multiplied by the coefficient of proportionality.

Now we will briefly survey the published theoretical models of surface segregation.   It is easily seen that the thermodynamical functions for random solution and for short range order solution reduce to the respective functions for an ideal solution when $\Omega \rightarrow 0$.   Equation (9) then becomes

$$RT \ln \frac{x_A^s(1-x_A)}{x_A(1-x_A^s)} + m(H_A^{sub}-H_B^{sub}) = 0.$$

Properties of this equation were discussed by Williams and Nason[15] and Overbury et al.[17]

Introducing the functions $\alpha_1(x_A)$ and $W(x_A)$ for a random solution into (9) yields the equation

$$RT \ln \frac{x_A^s(1-x_A)}{x_A(1-x_A^s)} + 2\Omega ZN_0[(\ell+m)x_A - \ell x_A^s - m/2] + m(H_A^{sub}-H_B^{sub}) = 0, \qquad (24)$$

which is equivalent to equations derived by Guggenheim[24] and Defay et al.[25] The surface concentration resulting from equation (24) was compared with that determined experimentally for alloys AgAu,[1,16,26] AgPd,[2] InPb.[17,26]

A process similar to surface segregation, namely the segregation of solute atoms to grain boundaries, was considered by McLean.[27] His expression for the equilibrium concentration of solute atoms at the boundary has the form

$$x_A^s = \frac{x_A \exp(E/RT)}{1-x_A+x_A \exp(E/RT)} \; , \qquad\qquad (25)$$

where $E = -\Delta U$ is the heat of segregation. Assuming that grain boundary corresponds to the surface of an alloy in vacuum it can be shown that expression (25) is equivalent to equation (24). Indeed, substituting (6) and (8) into (1) and introducing entropy of mixing for random solution we obtain expression (25). This equation was employed for discussion of surface properties of alloys AlCu[3] and AuNi.[6]

The surface composition in the case of multilayer model of surface region can be predicted analogously, although the respective derivation is much more extensive. The system of equations determining the composition of the first four surface layers was published by Williams and Nason [15] for the case of random solution. The interested reader is referred to this work. This model was compared with experimentally determined surface concentration of alloys CuNi,[15] AuNi,[13] NiPd,[10] AgAu,[26] InPb.[26] It was found[26] that the surface composition predicted by monolayer model is very close to composition of the first layer in the case of a four layer model. For this reason, as well as because of its complexity, the multi-layer model will not be given here.

(iii) Comparison of surface enrichment predicted by the
      first and second approximations.

As it follows from the brief review in the previous section, the exper-mental data on surface composition of binary metal alloys were compared only with surface composition resulting from the random solution model. It would be interesting to compare the surface enrichment predicted by both the random solution model and the short range order model, because the latter is supposed to describe the regular solution more accurately.

At the beginning let us consider functions $\alpha_1(x_A)$ and $\Delta s_m(x_A)$, since those functions introduce the main difference between both approaches. Both functions are symmetric in the range $0 < x_A < 1$ with respect to $x_A = 0.5$, having also their maximum value at this point. Figures 1 and 2 show the dependence of maximum values $\alpha_1(x_A=0.5)$ and $\Delta s_m(x_A=0.5)$ on the parameter Ω. The short range order parameter, α_1, turns out to be a nearly linear function of Ω/kT, having a slope close to 0.5. The molar entropy of mixing has its maximum value for $\Omega = 0$, i.e. for the ideal solution. As the absolute value of Ω/kT increases, the entropy of mixing gradually diminishes, although its dependence on Ω is not significant: Δs_m for $\Omega/kT = \pm 0.3$ differs from Δs_m for the random solution by not more than 10%.

The calculations of surface composition on the basis of equation (9) requires the knowledge of the number of first nearest neighbors, Z, Z_p, and Z_v. Those values for the low Miller index fcc and bcc surfaces are listed in Table II. The calculations in this section are performed for the fcc (111) surface, i.e. the values $Z = 12$, $\ell = 0.5$, $m = 0.25$ are used.

The surface composition calculated for both models using different values of Ω/kT and $\Delta H^{sub}/RT$ are presented in Table III. It can be seen that in a majority of the cases the short range order results in a decrease of the surface segregation in comparison with random solution when $\Omega < 0$. When $\Omega > 0$ the surface enrichment tends to be greater than that resulting from the random solution model. Although in some cases the difference reaches 50% ($\Omega/kT = 0.2$, $\Delta H^{sub} = 10$), the shape of the dependence of x_A^s on x_A seems to be the same, because the difference $x_A^s(2) - x_A^s(1)$ is usually much smaller than $x_A - x_A(1)$, especially for low values of Ω/kT. It is shown in Fig. 3 which presents the dependence of $x_A - x_A^s$ on x_A calculated for both models assuming

$\Omega/kT = 0.1$ and $\Delta H^{sub}/RT = 5$. In this case the difference $x_A^s(2) - x_A^s(1)$ is rather small, and does not exceed 15%.

As it was shown earlier, the value of Ω can be determined from expressions for coefficients of activity, i.e. from formulas (18) or (23). Evidently, both models will lead to different values of Ω from the same set of coefficients of activity, because different formulas are employed (Table I). Figure 4 compares the dependence of the coefficient of activity, γ_A, on x_A for both methods of calculation assuming $\Omega/kT = \pm 0.2$. The dependence of the coefficient of activity γ_B on concentration has the same shape, because in the case of both models the following relation holds: $\gamma_A(x_A) = \gamma_B(1-x_A)$. The difference between the values of γ_A calculated for random solution and for short range order solution is rather small; it does not exceed 10% in the whole range of concentrations. In the prevailing part of this range the coefficient of activity for the random solution is greater than that for the short range order solution, Ω being negative as well as positive. Conversely, the parameter Ω for a given alloy system, calculated from a certain set of activity coefficients, will always be smaller in the case of random solution than in the case of short range order solution. As it is easily seen, the deviation between both models shown in Figs. 3 and 4 are going to be added. It can lead to significant differences in some cases. For this reason in the next section, reviewing the experimental data on surface enrichment of both models will be employed in the discussion.

C. APPLICATION OF THE THEORY TO EXPERIMENTAL DATA

The development of Auger electron spectroscopy provided the powerful tool for investigation of the surface region of solids. The principles

of AES as well as the quantitative aspect were the subject of numerous review papers.[28-31]   This method enables the analysis of a surface region 1-10 atom layers deep.   The approximate formula connecting the measured intensity of Auger electrons having the energy E from an alloy, I_E, with concentration of component A in the surface region has the following form

$$I_E = k_E r_E \sum_{i=1}^{\infty} x_A^{(i)} \exp(-id/\lambda_E \cos\theta),$$

where k_E is a constant depending on properties of solid and instrumental parameters, r_E is the backscattering factor, $x_A^{(i)}$ is the concentration of component A in the i-th layer from the surface, d is the thickness of atom layer, λ_E is the escape depth of electrons varying from 4 Å to 30 Å in dependence on energy E (approximately proportional to $\sqrt{E}$), and θ is the acceptance angle of the analyzer.   Denoting the Auger electron current from the pure metal by I_E^o and assuming that k_E and r_E are independent of concentration of A, the following relation is obtained

$$I_E/I_E^o = \frac{\sum_{i=1}^{\infty} x_A^{(i)} \exp(-id/\lambda_E \cos\theta)}{\sum_{i=1}^{\infty} \exp(-id/\lambda_E \cos\theta)} . \qquad (26)$$

This formula can be further simplified by assuming that all Auger electrons are produced only in the first atom layer.   Then

$$I_E/I_E^o = x_A^{(1)} = x_A^s . \qquad (27)$$

Both formulas, (26) and (27), are employed in the calculation of the surface composition from Auger electron intensities.

The binary metal alloys in which the surface enrichment was found are listed in Table IV.   Seven of them have properties close to the regular solution model, i.e. AgAu, AgPd, AuCu, AuNi, CuNi, InPb and NiPd.   In temperatures of equilibration those systems form one phase solid solutions in the whole range of concentrations with the same crystallographic structure

as pure metals (fcc, with exception of the InPb system which was studied
in liquid state).   In all those systems the ratios of atom diameters is
contained in the range 1:1.26.   In the next sections the presented theory
will be compared with experimentally determined surface compositions for
those systems.   The thermodynamic data necessary for computation of the
surface composition were taken from tables published by Hultgren et al.[22,23]
Those values were chosen for temperatures as close to the experimental ones
as possible: T_H denotes the temperature for which the heats of sublimation
were chosen, and T_γ denotes the temperatures for which activity coefficients
were tabulated.   The Ω parameter was calculated as an arithmetical average
of its values calculated from all activity coefficients available on the
basis of equation (18) [$\Omega(1)$], or on the basis of equation (23) [$\Omega(2)$].   As
in the previous section, all calculations of the surface composition were
performed for (111) fcc surface plane unless otherwise stated.   In Figs.
5-10, showing the dependence of surface composition on the bulk composition,
solid line refers to the zeroth approximation (random solution model), dashed
line is for the first approximation (short range order model).

(i) The AgAu alloy

$T_H = 700$ K, $H_{Ag}^{sub} = 67\ 363$ cal/mole, $H_{Au}^{sub} = 87\ 480$ cal/mole.

$T_\gamma = 800$ K, $\Omega(1)/kT = -0.1757$, $\Omega(2)/kT = -0.1762$.

The resulting surface composition as a function of bulk composition is

shown in Fig. 5. The strong gold enrichment is predicted. In the same

plot the experimental values I/I^o are shown obtained for three Au Auger

electron energies: 69 eV (triangles), 239 eV (squares), 2024 eV (circles).[1]

The alloy was equilibrated in 673 K. Since the ratio I/I^o is to a first

approximation the surface concentration of Au, the experimental data show

also the Au surface enrichment but to a smaller extent than that predicted

by theory. The crosses represent surface composition of AgAu alloy

obtained by means of low-energy ion-scattering spectroscopy.[32] Those

values also indicate the smaller surface enrichment that is theoretical.

(ii) The AgPd alloy

$T_H = 1000$ K, $H_{Ag}^{sub} = 66\ 798$ cal/mole, $H_{Pd}^{sub} = 88\ 798$ cal/mole.

$T_\gamma = 1200$ K, $\Omega(1)/kT = -0.08404$, $\Omega(2)/kT = -0.08439$.

The surface compositon of the AgPd system is a subject of controversy.

Christmann and Ertl[33] did not find surface segregation by means of AES

in alloys equilibrated at 673 K. On the other hand, silver enrichment was

postulated by Bouwman et al.[34] in studies of the photoelectric work

function. The same conclusion results from infrared studies of carbon

monoxide adsorbed on AgPd alloys.[35] Mathieu and Landolt[36] found by AES

that the fractured AgPd alloys have a surface composition equal to bulk composition, whereas the sputtered alloys are enriched with palladium. However those results cannot be interpreted on the basis of the regular solution theory, because the surface region was obviously not in the equilibrium with the bulk. Wood and Wise[2] were using for quantitative analysis the same Auger electron transitions as Christmann and Ertl, i.e. $M_5N_{4,5}N_{4,5}$ transition of palladium (330 eV) and that of silver (351 eV). However, they equilibrated samples at a much higher temperature (975 K). The observed surface enrichment agrees reasonably well with theory, although once more the theory predicts stronger enrichment than that found experimentally (Fig. 6).

(iii) The AuCu alloy

$T_H = 700$ K, $H_{Au}^{sub} = 87$ 480 cal/mole, $H_{Cu}^{sub} = 80$ 014 cal/mole.

$T_\gamma = 800$ K, $\Omega(1)/kT = -0.2268$, $\Omega(2)/kT = -0.2184$.

The calculated surface composition is shown in Fig. 7.

McDavid and Fain[4] studied the surface composition of AuCu films evaporated at 673-723 K and then equilibrated at 573 K. The 69 eV, 239 eV and 2024 eV Auger electron energies were employed in the quantitative analysis. The experimentally determined composition of the first atom layer contradicts the theory prediction in the entire concentration range (Fig. 7). The considerable gold enrichment is observed although according to the theory, copper, as the metal having lower heat of sublimation, should segregate to the surface. The authors prescribed this effect to the large size difference between Au and Cu atoms, in agreement with the strain theory of surface segregation.[27]

(iv) The AuNi alloy

T_H = 1200 K, H_{Au}^{sub} = 86 569 cal/mole, H_{Ni}^{sub} = 101 265 cal/mole.

T_γ = 1150 K, $\Omega(1)/kT$ = 0.1633, $\Omega(2)/kT$ = 0.1638.

The theoretical surface composition is shown in Fig. 8. A considerable

gold enrichment is expected.   It was in fact observed by Williams and

Boudart[13] by means of AES.   They studied the Au electroplated poly-

crystalline nickel samples equilibrated at 1300 K using 145 eV Au and

848 eV Ni Auger electron energies.   A good agreement with theory can be

seen (Fig. 8), although in the case of nickel rich alloys the observed

enrichment is even greater than that predicted by theory.   Recently those

results were confirmed by Burton et al.[6].   They observed also a strong

surface enrichment with Au ($x_{Au}^s \cong$ 0.5-1.0, in dependence on heat treatment)

in the case of the alloy containing 1% Au.   Those authors were using low

energy Auger electron transitions: $N_7O_{4,5}O_{4,5}$ Au (69 eV), and $M_{2,3}M_{4,5}M_{4,5}$

Ni (61 eV), both being surface sensitive, because the escape depth of Auger

electrons having such energies is about 4 Å.

(v) The CuNi alloy

T_H = 1000 K, H_{Cu}^{sub} = 79 512 cal/mole, H_{Ni}^{sub} = 101 705 cal/mole.

T_γ = 973 K, $\Omega(1)/kT$ = 0.1223, $\Omega(2)/kT$ = 0.1227.

The CuNi system was found to have a miscibility gap with critical temperature

595 K.[37-39] For this reason the CuNi alloy has to be equilibrated well above

this temperature, where the system can be approximated by the regular solution

model.   There were numerous attempts to establish the surface composition

of the CuNi alloy since its catalytic properties are of considerable

interest.   Ertl and Küppers[40] and Quinto et al.[41] found that the

surface composition of annealed alloys is equal to the bulk composition.

Nakayama et al.[42] and Takasu and Shimizu[43] observed the dependence of the

surface composition on the treatment of the alloy. Ni or Cu segregation

was found in the case of Cu or Ni rich alloys respectively, equilibrated

in 573 K.[43] Nevertheless, the differences from bulk composition were not

significant. The referred investigators employed the high energy Auger electron

transitions in quantiative analysis: $L_3M_{2,3}M_{2,3}$ Ni (716 eV), $L_3M_{4,5}M_{4,5}$

Cu (920 eV), as well as overlapping transitions $L_3M_{2,3}M_{4,5}$ Cu (849 eV),

$L_3M_{2,3}M_{2,3}$ Cu (776 eV), $L_3M_{4,5}M_{4,5}$ Ni (848 eV) and $L_3M_{2,3}M_{2,3}$ Ni (775 eV).

Electrons having such energies escape from 5-8 atomic layers, which is

apparently more than the extent of surface segregation. Recently Helms[8]

and Helms and Yu[7] succeeded in resolving $M_1M_{4,5}M_{4,5}$ transitions at ~100 eV

(102 eV Ni and 105 eV Cu), originating from first 1-3 atom layers. Using

those peaks in quantitative analysis they found considerable surface enrichment

with copper of the (110) and (100) surfaces of the alloy single crystal,

equilibrated at 923 K. Their results are presented in Table V, and

compared with the surface concentrations resulting from theory for the

same surface planes.

Sinfelt et al.[44] studied the hydrogen adsorption on CuNi powders

equilibrated at 723 K. They also found the significant segregation of Cu

to the surface, especially in the low bulk Cu concentration region. The

5% Cu alloy was estimated to have 40-60% Cu on the surface.

(vi) The InPb alloy

T_H = 800 K, H_{In}^{sub} = 56 461 cal/mole, H_{Pb}^{sub} = 44 503 cal/mole.

T_γ = 673 K, $\Omega(1)/kT$ = 0.03719, $\Omega(2)/kT$ = 0.03723.

In those temperatures the alloys is liquid in the whole concentration

range. Figure 9 shows the ratio x_{Pb}^s/x_{In}^s resulting from the theory as a

function of x_{Pb}/x_{In}. The Pb surface enrichment is expected.

Berglund and Somorjai[9] studied the series of liquid InPb alloys by means of AES. The strongest Auger electron transitions were chosen for surface analysis: $N_7O_{4,5}O_{4,5}$ Pb(92 eV) and $M_5N_{4,5}N_{4,5}$ In (403 eV). The ratios of intensities of Auger electrons from alloys, I^o_{Pb}/I^o_{In}, divided by the same ratio of intensities from pure metals, I^o_{Pb}/I^o_{In}, all recorded in 773 K, are shown in Fig. 9. Those quantities to a first approximation are equal to x^s_{Pb}/x^s_{In}. The surface enrichment can be observed, but not to the extent that is predicted by theory.

(viii) The NiPd alloy

T_H = 1200 K, H^{sub}_{Ni} = 101 265 cal/mole, H^{sub}_{Pd} = 88 385 cal/mole.

T_γ = 1273 K, $\Omega(1)/kT$ = -0.07736, $\Omega(2)/kT$ = -0.07953.

Mathieu and Landolt[36] found that fractured alloys have surface composition equal to bulk composition, whereas the extensively sputtered surface is enriched with nickel. For quantitative analysis they used $M_5N_{4,5}N_{4,5}$ Pd transition (330 eV), and $L_3M_{4,5}M_{4,5}$ Ni transition (848 eV). Those results cannot be compared with the regular solution theory prediction, because the surface was not equilibrated with the bulk. Stoddart et al.[10] determined the surface composition of thin NiPd films using, in addition to high energy Auger electron transitions, the $M_{2,3}M_{4,5}M_{4,5}$ Ni transition (61 eV), and $N_{2,3}N_{4,5}N_{4,5}$ Pd transition (43 eV). A considerable Pd enrichment was observed. Under evaporation conditions the film temperature was estimated to be less than 640 K. Unfortunately, it is impossible to calculate the surface composition at this temperature because the only existing values of activity coefficients are tabulated for 1200 K. Also, it is probable that the surface in this case was not fully equilibrated, which means that

the enrichment may be even stronger.   Nonetheless, in Fig. 10 the values
of surface composition obtained by Stoddart et al. are compared with
results of calculations for 1200 K to show that the direction surface
segregation is the same as that predicted by theory.

D.   CONCLUSION

In all the alloy systems discussed above, the surface enrichment
calculated for the short range order model is close to the enrichment
resulting from the random solution model, even in the case of alloys having
large value of the Ω parameter (AgAu, AuNi).   The relative difference of
surface concentrations calculated for both models $[x_A^S(2)-x_A^S(1)]/x_A^S(2)$, is
about 50% in those cases, but the shape of the dependence of x_A^S on x_A is
almost the same.   The difference $x_A^S(2)-x_A(1)$ is rather small and does not
exceed 0.07 for the AgAu system, 0.03 for the AuNi system, and 0.02 for
the AgPd system in the whole concentration range.   Also, the ratio of
this difference to the bulk concentration, x_A, never exceeds 10%.   Overbury
and Somorjai[1] considered the short range order in the AgAu alloy as a
possible cause of the considerable deviations between experimentally
determined surface composition and the prediction of the regular solution
theory (zeroth approximation).   This explanation is not feasible on the
basis of calculations presented in this paper.

As if follows from the previous section, the regular solution theory
in six cases out of seven predicted the experimentally observed surface
enrichment.   However, the theory is far from the precise prediction of the
surface composition; the experimentally determined surface concentrations
usually deviate considerably from concentration calculated on the basis of
both the random solution model and the short range order model.   The

differences $x_A^S(exp)-x_A^S(calc)$ are within the ranges: 0.10-0.38 for the

AgAu alloy, 0.13-0.25 for the AgPd alloy, 0.01-0.50 for the AuNi alloy,

and 0.01-0.32 for the CuNi alloy.   Those differences may result from

rather severe simplifications, made in the regular solution model, e.g.

taking into account only the first nearest neighbors interaction, neglecting

the vibrational, electronic and magnetic contributions to the entropy of

mixing, assuming the constant value of the Ω parameter in the whole concen-

tration range, assuming the thermodynamical equivalence of the surface region

with the bulk.   Another cause of deviations may also be the imperfection

of quantitative analysis by AES.   In most of the alloy systems considered,

AgAu, AgPd, InPb and CuNi, the calculated surface enrichment was stronger

than that observed experimentally.   It is probable that the simplifications

made in the regular solution model lead to overestimating the extent of

the surface segregation.

The regular solution theory does not take into account surface

segregation resulting from strain caused by the different sizes of metal

atoms.   According to the strain theory, the atom having greater diameter

will segregate to the surface.[27]   Among the metal alloys discussed, the

greatest difference in atom sizes is in the AuNi and AuCu alloys.   The

ratio of atom diameters, Au to Ni and Au to Cu, is equal to 1.16 and 1.13,

respectively.   In the case of the AuNi alloy the gold segregation is

predicted by both the regular solution theory and the strain theory.   The

observed surface enrichment is considerably larger than that predicted by

the regular solution theory, especially in the nickel rich region, where

the gold atoms cause the strongest strain.   The strain can also be

partially responsible for the observed Au segregation in the AuCu alloy.

In conclusion, the regular solution theory enables the prediction of the element which will segregate to the surface in most metal binary alloys and, bearing in mind the limitations of theory, gives reasonably good agreement with experimental results.

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FIGURE CAPTIONS

Fig. 1.   The dependence of the maximum value of the short range order

parameter on the parameter Ω.

Fig. 2.   The dependence of the maximum value of the configurational entropy

of mixing on the parameter Ω.

Fig. 3.   The surface composition as a function of bulk composition calculated

for an alloy with $\Delta H^{sub}/RT = 5$ and $\Omega/kT = \pm 0.1$ The solid line –

zeroth approximation (random solution model); the dashed line –

first approximation (short range order model).

Fig. 4.   The dependence of the activity coefficient, γ_A, on alloy composition.

The solid line – zeroth approximation; the dashed line – first

approximation.

Fig. 5.   The surface composition as a function of bulk composition calculated

for the AgAu alloy; T = 700 K.   Experimental values: Overbury

and Somorjai[1] (Δ – I_{69}/I^0_{69}, $\square$ – I_{239}/I^0_{239}, o – I_{2024}/I^0_{2024});

Nelson[32] ($\times$).

Fig. 6.   The surface composition as a function of bulk composition calculated

for the AgPd alloy; T = 1000 K.   Experimental values: Wood and

Wise.[2]

Fig. 7.   The surface composition as a function of bulk composition calculated

for the AuCu alloy; T = 700 K.   Experimental values: McDavid and

Fain.[4]

Fig. 8.   The surface composition as a function of bulk composition calculated

for the AuNi alloy; T = 1200 K.   Experimental values: Williams

and Boudart.[13]

Fig. 9.   The dependence of the ratio of surface concentrations, x_{Pb}^s/x_{In}^s,

on the same ratio of bulk concentrations, x_{Pb}/x_{In}; T = 800 K.

Experimental values: Berglund and Somorjai.[9]

Fig. 10.   The surface composition as a function of bulk composition calculated

for the NiPd alloy; T = 1200 K.   Experimental values: Stoddart

et al.[10]

Table I. The functions $\alpha_1(x_A)$, $W(x_A)$ and Ω parameter for the regular solution.

Random solution (zeroth approximation)	Short range order solution (first approximation)
The short range order parameter $\alpha_1(x_A)$	
$\alpha_1(x_A) = 0$	$\alpha_1(x_A) = (\beta-1)/(\beta+1)$
The function $W(x_A)$	
$W(x_A) = -R \ln[x_A/(1-x_A)]$	$W(x_A) = -R \ln[x_A/(1-x_A)]$ $- \tfrac{1}{2}ZR \ln \dfrac{(\beta-1+2x_A)(1-x_A)}{(\beta+1-2x_A)x_A}$ $+ Z\Omega N_o(1-2x_A)/T\beta$ where $\beta = [1+4x_Ax_B(\exp(2\Omega/kT) - 1)]^{\frac{1}{2}}$
The relation of Ω parameter to the coefficient of activity	
$\Omega N_o = RT \ln(\gamma_A)/Z(1-x_A)^2$ $= RT \ln(\gamma_B)/Zx_A^2$	$\Omega N_o = \tfrac{1}{2}RT \ln \left(\dfrac{\beta^2-1}{4x_A(1-x_A)} + 1 \right)$ where $\beta = \dfrac{2(1-x_A)}{1-x_A\gamma_A^{2/Z}} - 1$ or $\beta = \dfrac{2x_A}{1-(1-x_A)\gamma_B^{2/Z}} - 1$
The relation of Ω parameter to the molar heat of mixing, Δu_m	
$\Omega N_o = \Delta u_m/Zx_A(1-x_A)$	$\Omega N_o = RT\xi$ where $y = \xi$ is the root of equation $RTZCy - \Delta u_m\{[1+2C(\exp(2y)-1)]^{\frac{1}{2}} +1\} = 0$ $C = 2x_Ax_B$

Table II.   The numbers of first nearest neighbors for the low Miller index fcc and bcc surfaces.

Surface	Z	Z_p	Z_v	ℓ	m
Face centered cubic					
(100)	12	4	4	0.333	0.333
(110)	12	2	5	0.167	0.417
(111)	12	6	3	0.5	0.25
Body centered cubic					
(100)	8	0	4	0	0.5
(110)	8	4	2	0.5	0.25
(111)	8	0	4	0	0.5

Table III. Comparison of surface concentrations $x_A^s(1)$ and $x_A^s(2)$, calculated on the basis of zeroth and first approximations, respectively, for the (111) fcc surface.

Ω/kT	-0.2		-0.1		0	0.1		0.2	
	$x_A^s(1)$	$x_A^s(2)$	$x_A^s(1)$	$x_A^s(2)$	$x_A^s(1)=x_A^s(2)$	$x_A^s(1)$	$x_A^s(2)$	$x_A^s(1)$	$x_A^s(2)$
					$\Delta H^{sub}/RT = 5$				
0.2	0.065	0.074	0.066	0.071	0.067	0.068	0.062	0.070	0.056
0.4	0.211	0.230	0.188	0.201	0.160	0.127	0.111	0.093	0.066
0.6	0.425	0.436	0.374	0.384	0.301	0.200	0.178	0.104	0.072
0.8	0.684	0.689	0.628	0.628	0.534	0.361	0.354	0.141	0.111
					$\Delta H^{sub}/RT = 7$				
0.2	0.042	0.053	0.042	0.047	0.042	0.041	0.035	0.041	0.029
0.4	0.156	0.185	0.131	0.148	0.104	0.077	0.062	0.053	0.033
0.6	0.349	0.368	0.287	0.302	0.207	0.121	0.099	0.059	0.036
0.8	0.611	0.609	0.534	0.531	0.410	0.226	0.211	0.079	0.059
					$\Delta H^{sub}/RT = 10$				
0.2	0.021	0.031	0.021	0.025	0.020	0.019	0.015	0.019	0.011
0.4	0.092	0.131	0.071	0.090	0.052	0.036	0.026	0.024	0.012
0.6	0.245	0.280	0.178	0.202	0.110	0.057	0.041	0.027	0.013
0.8	0.495	0.481	0.391	0.388	0.247	0.107	0.089	0.035	0.021

Table IV.   Surface segregation of binary metal alloys by AES.

Author(s)	System	Bulk concentration range	Temperature of equilibration K	Object	Surface enrichment
Overbury, Somorjai[1]	Ag-Au	whole range	673	polycrystalline alloy foils	Ag
Wood, Wise[2]	Ag-Pd	<40%	975	alumina supported alloy catalysts	Ag
Ferrante[3]	Al-Cu	<10% Al	473-973	(111) face of alloy single crystals	Al
McDavid, Fain[4]	Au-Cu	whole range	573	alloy films	Au
Thomas[5]	Au-In	2% In	room temperature	alloy films	In
Williams, Boudart[13]	Au-Ni	<36% Au	1300	Au electrodeposited on Ni foil and annealed	Au
Burton, Helms Polizzotti[6]	Au-Ni	<1% Au	<1273	vapor deposited Au onto (111) Ni and annealed	Au
Helms, Yu[7] Helms[8]	Cu-Ni	10% and 50% Cu	923	(100) and (110) single crystal faces	Cu
Seah, Lea[14]	Fe-Sn	<1% Sn	823-1693	polycrystalline samples	Sn
Berglund, Somorjai[9]	In-Pb	<60% Pb	773	liquid alloys	Pb
Stoddart, Moss, Pope[10]	Ni-Pd	whole range	after vapor deposition at room temperature	thin alloy films	Pd
Leygraf, Hultquist Ekelund, Eriksson[11]	Fe-Cr	16% Cr	675-1175	(100) and (110) faces of alloy single crystal	Cr
Bouwman, Toneman, Holscher[12]	Pt-Sn		773	polycrystalline compounds PtSn and Pt_3Sn	Sn

Table V. Comparison of theoretical and experimentally determined[7] surface compositions
of CuNi alloys. The surface concentrations were calculated for 1000 K.

Bulk Composition x_{Ni}	Orientation	Experimental surface composition x_{Ni}^{s}	The theory prediction	
			Random solution $x_{Ni}^{s}(1)$	Short range order solution $x_{Ni}^{s}(2)$
0.50	(100)	0.0	0.015	0.009
0.90	(100)	0.35±0.10	0.061	0.052
0.90	(110)	0.35±0.10	0.033	0.028

Fig. 1

Fig. 2

Fig. 3

XBL769-7550

Fig. 4

Fig. 5

XBL 769-7553

Fig. 6

XBL 769-7554

Fig. 7

XBL 769–7555

Fig. 8

Fig. 9

XBL 769-7556

XBL 769-7557

Fig. 10