

## Prediction of Segregation to Alloy Surfaces from Bulk Phase Diagrams

J. J. Burton

*Exxon Research and Engineering Company, Linden, New Jersey 07036*

and

E. S. Machlin

*Columbia University, New York, New York 10027*

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Current theories of surface segregation are based on either the difference in the sizes or the heats of sublimation of the alloy components. We show that neither of these theories gives adequate agreement with experiment. A simple rule, based on the melting curve of the alloy, gives good agreement with all available experimental data.

Gibbs<sup>1</sup> predicted a century ago that the equilibrium composition of an alloy surface is not necessarily identical to its bulk composition; that is, one component of the alloy may segregate to its surface. This phenomenon, known as surface segregation, has considerable importance in metallurgy<sup>2</sup> and catalysis<sup>3</sup> and has attracted recent interest.<sup>4</sup> In this Letter, we show how to predict the surface segregation behavior of alloys.

Rigorously, the excess surface concentration of one component of an alloy over its bulk concentration,  $\Gamma$ , is related to the composition dependence of the surface tension  $d\sigma/da$  by<sup>5</sup>

$$\Gamma = -(a/RT)(d\sigma/da). \quad (1)$$

This means that one component of the alloy should segregate to its surface if the surface tension decreases with increasing concentration of that component. The problem in applying Gibb's rigorous result is that generally very little is known about the composition dependence of the surface tension,  $d\sigma/da$ . Therefore, a number of alternative approaches to prediction of surface segregation have been attempted.<sup>3,6-9</sup> For very dilute binary alloys, the surface concentration of the solute,  $X_s$ , is related to its bulk concentration,  $X_B$ , by

$$\frac{X_s}{1-X_s} = \frac{X_B}{1-X_B} e^{Q/RT}, \quad (2)$$

where  $Q$  is the heat of segregation. If  $Q$  is large and positive, then segregation should occur. Two approaches to estimate  $Q$  were suggested. One is based on bond breaking and predicts that the lower heat of sublimation component of the alloy should segregate to its surface<sup>7-9</sup>; here the driving force for segregation is envisioned as maximization of the number of the strong bonds in the system. The second is based on elastic strain

and predicts that segregation should occur whenever the size difference between the constituents is large<sup>6</sup>; here the driving force for segregation is the lowering of the elastic strain energy in the bulk which arises from lattice mismatch. Both of these theories of surface segregation have proven useful in interpreting catalytic and metallurgical phenomenon.

Recently, reliable measurements have been made of the heat of segregation,  $Q$ , in a number of very clean dilute binary alloy systems in vacuum. The results are shown in Table I. The quantitative agreement between theory and experiment is quite bad. The size-difference theory does not even predict segregation of Au to the Pt surface, while it does occur. Similarly, the bond-breaking theory gives badly wrong results for Fe(Zr) and both theories fail for Pt(Ni) and Pt(Fe).

As the theories are obviously quantitatively unsatisfactory, it is appropriate to compare the qualitative predictions of the two theories with

TABLE I. Comparison of measured and predicted heats of segregation,  $Q$ .

Solvent (solute)	Q (kcal/mole)		
	Experiment	Theory	
		Bond breaking	Size difference
Ni(Au) <sup>a</sup>	12	4	9
Zr(Fe) <sup>b</sup>	17	12	9
Fe(Zr) <sup>b</sup>	> 30	-12	20
Pt(Ni) <sup>c</sup>	0	8	5
Pt(Fe) <sup>c</sup>	0	9	4
Pt(Cr) <sup>c</sup>	0	10	2
Pt(Au) <sup>d</sup>	> 10	12	0

<sup>a</sup>Ref. 10.

<sup>b</sup>Ref. 11.

<sup>c</sup>Ref. 12.

<sup>d</sup>Ref. 13.

TABLE II. Comparison of the predicted and observed segregation behavior in several systems. The question asked is "Does segregation of the solute to the solvent surface occur?" and the answer given is either Yes (Y) or No (N). Summary: Bond breaking is wrong six times out of sixteen. Size difference is wrong seven times out of sixteen.

Solvent (solute)	Does segregation occur?		
	Experiment	Theory	
		Bond breaking	Size difference
Ag(Au) <sup>a</sup>	N	N	N
Au(Ag) <sup>b</sup>	Y	Y	N
Cu(Au) <sup>c</sup>	Y	N	Y
Fe(Cr) <sup>d</sup>	Y	N	N
Fe(Sn) <sup>e</sup>	Y	Y	Y
Fe(Zr) <sup>f</sup>	Y	N	Y
Ni(Au) <sup>g</sup>	Y	Y	Y
Ni(Cu) <sup>h</sup>	Y	Y	N
Pd(Au) <sup>i</sup>	N	N	N
Pd(Ag) <sup>i</sup>	Y	Y	N
Pt(Au) <sup>j</sup>	Y	Y	N
Pt(Cr) <sup>k</sup>	N	Y	N
Pt(Fe) <sup>k</sup>	N	Y	Y
Pt(Ni) <sup>k</sup>	N	Y	Y
Pt(Sn) <sup>l</sup>	Y	Y	Y
Zr(Fe) <sup>f</sup>	Y	Y	Y

<sup>a</sup>Ref. 15.

<sup>b</sup>Refs. 15-17.

<sup>c</sup>Ref. 18.

<sup>d</sup>Ref. 19.

<sup>e</sup>Ref. 20.

<sup>f</sup>Ref. 11.

<sup>g</sup>Refs. 10 and 21.

<sup>h</sup>Refs. 22 and 23.

<sup>i</sup>Ref. 24.

<sup>j</sup>Ref. 13.

<sup>k</sup>Ref. 12.

<sup>l</sup>Ref. 25.

experimental results on a wide range of systems. We can simply ask "Does segregation of the solute to the surface occur?" and compare the experimental results with the theoretical predictions. This comparison is summarized in Table II.<sup>14</sup> Neither theory does very well; both disagree with nearly half of the experiments.

The results in Table II indicate that the current theories of surface segregation are frequently wrong. This conclusion is not entirely surprising, because both of these theories of surface segregation are essentially microscopic theories. While they have proven useful in rationalizing metallurgical and catalytic phenomena, they really cannot be expected to be generally applicable. Surface segregation is basically a phase-diagram sort of problem and microscopic theories have proven notoriously unreliable for predicting complex alloy phase diagrams. We propose here a new approach to predicting segregation based on bulk alloy phase diagrams.

We suggest that surface segregation is related to equilibrium distribution of a solute in an alloy to its liquid. This appears reasonable since

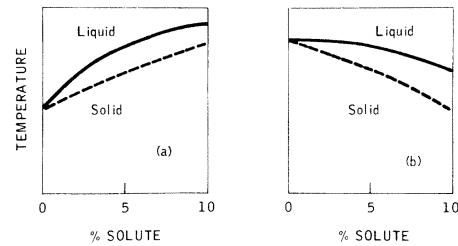


FIG. 1. Typical phase diagrams for dilute alloys. The region between the solidus (dashed curve) and the liquidus (solid curve) is a two-phase region. Here solid and liquid (with different compositions) co-exist. For melting curves in (a), solute *does not* distribute from the solid to the liquid and the solute *does not* segregate from the solid to its surface. For melting curves as in (b), solute *does* distribute from the solid to the liquid and solute *does* segregate from the solid to its surface.

many of those aspects which distinguish a liquid from a solid—lower symmetry, lower coordination, and no elastic strain—also distinguish a solid from a surface. Therefore, we *posit* that segregation should occur in the solid/surface equilibrium if and only if distribution occurs in the solid/liquid equilibrium so that the liquid is richer in solute than the solid phase. The point of this approach is that solute distribution between a liquid and solid is well understood; in fact, it is the basis for zone-refining to produce ultrahigh-purity solids.

In Fig. 1 are shown the two types of solid/liquid equilibrium curves which are the basis for predicting distribution of solute from the solid to the liquid or segregation from the solid to the surface. Figure 1(b) represents a segregating or distributing system. If a solid containing 5% solute were heated to its solidus temperature (dashed curve), liquid would begin to form containing a solute concentration of about 10%; thus, solute would distribute from the solid to the liquid. If a 5% alloy of the nondistributing system [Fig. 1(a)] were heated to its solidus temperature, the liquid formed would contain only about 2% solute; thus, solute distribution from the solid to the liquid would not occur.

Following our analogy between solid/liquid and solid/surface equilibria, we propose that any dilute binary alloy with a melting curve like Fig. 1(a) should show no segregation. Those with melting curves such as in Fig. 1(b) can show surface segregation. Since, in our picture, the driving force for segregation in a type-b alloy [Fig. 1(b)] is related to the separation between the soli-

TABLE III. Comparison of experimental surface-segregation results and predictions based on the phase diagrams (Ref. 26). The alloys are divided into three types: Type-b are those with melting curves like Fig. 1(b) and large separation between the solidus and the liquidus. Type-b' alloys also have melting curves like Fig. 1(b) but the separation between the solidus and the liquidus is small. Type-a alloys have melting curves like Fig. 1(a). Type-b alloys are expected to show segregation. Type-b' and type-a alloys are expected to show little or no segregation.

Solvent (solute)	Does segregation occur?	Melting curve type
Au(Ag) <sup>a</sup>	Yes	b
Cu(Au) <sup>b</sup>	Yes	b
Fe(Cr) <sup>c</sup>	Yes	b
Fe(Sn) <sup>d</sup>	Yes	b
Fe(Zr) <sup>e</sup>	Yes	b
Ni(Au) <sup>f</sup>	Yes	b
Ni(Cu) <sup>g</sup>	Yes	b
Pd(Ag) <sup>h</sup>	Yes	b
Pt(Au) <sup>i</sup>	Yes	b
Pt(Sn) <sup>j</sup>	Yes	b
Zr(Fe) <sup>e</sup>	Yes	b
Ag(Au) <sup>k</sup>	No	a
Pd(Au) <sup>h</sup>	No	b'
Pt(Cr) <sup>l</sup>	No	b'
Pt(Fe) <sup>l</sup>	No	b'
Pt(Ni) <sup>l</sup>	No	b'

<sup>a</sup>Refs. 15-17.

<sup>b</sup>Ref. 18.

<sup>c</sup>Ref. 19.

<sup>d</sup>Ref. 20.

<sup>e</sup>Ref. 11.

<sup>f</sup>Refs. 10 and 21.

<sup>g</sup>Refs. 22 and 23.

<sup>h</sup>Ref. 24.

<sup>i</sup>Ref. 13.

<sup>j</sup>Ref. 25.

<sup>k</sup>Ref. 15.

<sup>l</sup>Ref. 12.

and the liquidus, we would expect that, if this separation is large then copious surface segregation should occur, but if it is small very little surface segregation should occur. The application of these rules using published real phase diagrams<sup>26</sup> is straightforward.

Our predictions for the alloys of Table II using these rules are summarized in Table III. The agreement between the predictions of this simple model and experiment are strikingly good. All of the alloys studied to date with type-b melting curves [Fig. 1(b)] and large separation between the solidus and liquidus show surface segregation. Those with either type-a melting curves [Fig. 1(a)] or type-b curves [Fig. 1(b)] but small separation between the solidus and the liquidus (i.e., type-b' in Table III) show no segregation.

It is thus clear that surface-segregation behavior in vacuum can be adequately predicted from very simple considerations of the shapes of the bulk melting curves of the dilute solutions. Al-

loys with phase diagrams in the dilute limit like Fig. 1(b) are expected to segregate solute to the surface if the separation between the solidus and the liquidus is large, while those with small separation between the solidus and liquidus or like Fig. 1(a) will not show segregation.

<sup>1</sup>J. W. Gibbs, *Trans. Conn. Acad. Arts Sci.* **3**, 108 (1875/76), 343 (1877/78).

<sup>2</sup>M. P. Seah, *Surf. Sci.* **53**, 168 (1975).

<sup>3</sup>J. J. Burton and E. Hyman, *J. Catal.* **37**, 114 (1975).

<sup>4</sup>S. H. Overbury, P. A. Bertrand, and G. A. Somorjai, *Chem. Rev.* **75**, 547 (1975).

<sup>5</sup>A. W. Adamson, *Physical Chemistry of Surfaces* (Wiley, New York, 1967).

<sup>6</sup>D. McLean, *Grain Boundaries in Metals* (Clarendon, Oxford, 1957).

<sup>7</sup>F. L. Williams and D. Nason, *Surf. Sci.* **45**, 377 (1974).

<sup>8</sup>R. A. Van Santen and W. M. H. Sachtler, *J. Catal.* **33**, 202 (1974).

<sup>9</sup>J. J. Burton, E. Hyman, and D. Fedak, *J. Catal.* **37**, 106 (1975).

<sup>10</sup>J. J. Buron, C. R. Helms, and R. S. Polizzotti, *J. Vac. Sci. Technol.* **13**, 204 (1976).

<sup>11</sup>R. S. Polizzotti and J. J. Burton, to be published.

<sup>12</sup>J. J. Burton and R. S. Polizzotti, to be published.

<sup>13</sup>J. A. Schwarz, R. S. Polizzotti, and J. J. Burton, to be published.

<sup>14</sup>We have included in Table II only results obtained on very clean surfaces since we have shown that impurities can significantly alter segregation behavior [Ref. 10, and J. J. Burton, C. R. Helms, and R. S. Polizzotti, *J. Chem. Phys.* **65**, 1089 (1976)]. Where different workers have obtained different results, as in Ni(Cu) [G. Ertl and J. Kuppers, *Surf. Sci.* **24**, 104 (1971); C. R. Helms and K. Y. Yu, *J. Vac. Sci. Technol.* **12**, 276 (1975); C. R. Helms, *J. Catal.* **36**, 114 (1975)] and Pd(Ag) [K. Christmann and G. Ertl, *Surf. Sci.* **33**, 254 (1972); B. J. Wood and H. Wise, *Surf. Sci.* **52**, 151 (1975)], we have generally believed the worker reporting segregation, because it is easy to fail to see segregation when it should occur due to poor technique or inadequate annealing of the sample, but difficult to see it if it does not occur. We have also tended to prefer results on dilute alloys over concentrated alloys. We have also somewhat arbitrarily stated that the bond-breaking theory predicts segregation if the heat of sublimation of the solvent exceeds that of the solute by more than 15 kcal/mole, which would imply a heat of segregation of about 4 kcal/mole. Similarly, we arbitrarily state that the size-difference theory predicts segregation for size differences greater than about 10%, which would imply a heat of segregation of about 4 kcal/mole in a typical system.

<sup>15</sup>G. A. Somorjai and S. H. Overbury, *Surf. Sci.* **55**, 209 (1976).

<sup>16</sup>G. C. Nelson, *J. Vac. Sci. Technol.* **13**, 512 (1976).

<sup>17</sup>G. C. Nelson, to be published.

<sup>18</sup>J. M. McDavid and S. C. Fain, *Surf. Sci.* **52**, 161

(1975).

<sup>19</sup>C. Leygraf, G. Hultquist, S. Ekelund, and J. C. Ericksson, *Surf. Sci.* **46**, 157 (1974).<sup>20</sup>M. P. Seah and C. Lea, *Philos. Mag.* **31**, 627 (1975).<sup>21</sup>Burton, Helms, and Polizzotti, Ref. 14.<sup>22</sup>Helms and Yu, Ref. 14.<sup>23</sup>Helms, Ref. 14.<sup>24</sup>Wood and Wise, Ref. 14.<sup>25</sup>R. Bouwmann, L. H. Toneman, and A. A. Holscher, *Surf. Sci.* **35**, 8 (1973).<sup>26</sup>M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958).

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 COMMENTS
 

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**Polarization of Prompt Muons Produced at  $P_t = 2.15$  GeV/ $c$  by 400-GeV Proton Interactions\***

M. J. Lauterbach, R. K. Adair, A. B. Carter, D. M. Grannan,  
H. Kasha, R. G. Kellogg, and M. P. Schmidt  
*Yale University, New Haven, Connecticut 06520*

and

L. B. Leipuner and R. C. Larsen  
*Brookhaven National Laboratory, Upton, New York 11973*  
(Received 23 September 1976)

The polarization of prompt muons produced at a center-of-mass angle of  $61^\circ$  and a transverse momentum of  $2.15$  GeV/ $c$  by the interaction of 400-GeV protons was measured to be  $-0.135 \pm 0.20$ . This value, consistent with zero, differs from the large value reported from similar measurements at 70 GeV and is inconsistent with the proposal that the prompt leptons observed at large transverse momenta are derived from weak decays of intermediate particles.

It has been proposed<sup>1</sup> that the anomalously large production of prompt leptons at large values of  $p_t$  by nucleon-nucleon interactions might be derived from the weak decays of intermediate particles. Most plausible descriptions of such decays would lead to a large polarization of leptons so produced along their direction of flight. Recent communications by Anisimova *et al.*<sup>2</sup> and Abramov *et al.*<sup>3</sup> report measurements of the polarization of prompt muons produced by the interaction of 70-GeV protons with nuclei. They find a value of  $-0.85 \pm 0.37$  for the polarization of positive muons produced at an angle of  $90^\circ$  in the center-of-mass system with transverse momenta of 2.0 and 2.8 GeV/ $c$ . Such a result, indeed any value of the longitudinal polarization other than zero, indicates that the production must be mediated by a parity-nonconserving interaction.

We have now made similar measurements at Fermilab of the longitudinal polarization of prompt muons produced with transverse momenta of 2.15 GeV/ $c$  by the interaction of 400-GeV protons with nuclei. Muons, produced through the interaction of protons with a variable-density

copper target, passed through the target and through steel shielding near the target with trajectories defined by counters set 60 m from the target at an angle of  $45$  mr from the proton beam direction. The muons then passed through 60 m of earth to stop in a polarimeter designed to measure the polarization of the muons in the direction of their flight and the component of polarization perpendicular to the plane of production. The characteristics of the target and a more complete description of the beam have been presented previously.<sup>4</sup>

The energy of the muons was defined by their range as  $54 \pm 2$  GeV. While the mean transverse momentum of the muons emerging from the target assembly was then about 2.40 GeV/ $c$ , the mean production transverse momenta was calculated to be  $2.15 \pm 0.10$  GeV/ $c$  when the effects of the multiple scattering of the muons by the material of the target assembly were considered; the muon angle of production in the center-of-mass system of the nucleon-nucleon interaction was then  $61^\circ$ .

The polarimeter consisted, basically, of 24