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Reply to Comment on

“On the relationship between the entropy and enthalpy of interfacial segregation” by P. Lejček and S. Hofmann

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Abstract. This note aims to resolve some terminological misunderstanding reflected by the comment of Lejček and Hofmann (L-H). It stems primarily from the difference in two reference systems quite commonly used in the description of interfacial segregation. Our article referred to an ideal solution defined atomistically by equal interactions between all constituents, that exhibits ideal behavior (in accordance with Raoult's law) over all concentrations, no change of internal energy on mixing or demixing, and therefore, the absence of any segregation “driving force”. The use of such ideal solution as a reference system to excess thermodynamical properties, *e.g.*, the “excess free energy of segregation”, is fully consistent with common basic definitions and previous works. The different reference system inherent in the approach used by L-H (in accordance with early segregation theories) is based on the infinitesimally dilute solution approximation (Henry's law region), and is the source of the terminological disagreement regarding the actual meaning of excess properties.

PACS. 05.70.Np Interface and surface thermodynamics – 64.75.+g Solubility, segregation, and mixing; phase separation

The main goal of our paper was to point out the identity of one parameter, the intercept (σ) in the reported entropy/enthalpy linear relationship, namely, that it is just the negative value of the ideal configurational entropy of segregation in A_cB_{1-c} alloys, $\sigma = k \ln \frac{c_0(1-c)}{c(1-c_0)}$, where c_0 and c denote the surface and bulk solute concentration, respectively.

While this simple physical meaning of the parameter was not mentioned in Lejček and Hofmann's (L-H) previous papers, their present Comment is focused almost entirely on subtle terminological matters, causing certain confusion in the literature, which we try to clarify in this short Reply. In particular, we used the term “excess” as is quite commonly accepted (also by the referee), *i.e.* as the difference between the thermodynamic functions of “real” and “ideal” systems [1] (an unambiguous definition was given in our paper and the review [2] mentioned by L-H). In view of the arguments raised in the Comment, the following concepts deserve some elucidation:

1. Strictly speaking, we referred to an ideal solution with equal interactions between all constituents, A-A, B-B and A-B (*e.g.*, Refs. [3–6])[1], and hence the absence of any segregation “driving force”, $\Delta G = 0$, in the Langmuir-McLean type equation for the alloy surface composition,

$$\frac{c_0}{1-c_0} = \frac{c}{1-c} \exp\left(-\frac{\Delta G}{kT}\right).$$

Such solutions exhibit ideal behavior (in accordance with Raoult's law) over all concentrations, and no change of internal energy on mixing (or demixing, including segregation).

2. In real solutions, having unequal interatomic interactions, a non-zero ΔG, which in principle can be concentration and temperature dependent, is denoted by the “excess free energy of segregation”, ΔG^{ex} (*e.g.*, [9–12]), consistently with its role in inducing surface excess in a constituent concentration.

3. With increasing dilution, real solutions start to behave close to “ideality” (Henry's law region for the solutes). L-H adopted quite an early formalism [13], that

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[1] This useful definition of an “ideal solution”, sometimes termed “perfect solution” [7] or Lewis-Randall “ideal mixture”, has become quite customary as a reference system [8].

is consistent with this dilute limit approximation, and according to which ΔG is divided into a concentration-independent term, "*standard molar Gibbs free energy of segregation*", ΔG^0, describing "*infinitesimally diluted* (*non-interacting*) *binary systems*", and an additional "*excess*" contribution.

It should be noted, however, that attributing "ideality" to ΔG^0 is inconsistent with the former (more strict) definition (#1) of an ideal solution, since the absence of interactions is confined in the dilute limit to A-A (solute-solute) pairs only, and upon segregation ($\Delta G^0 \neq 0$) the internal energy does change. Furthermore, segregated interfaces are often non-dilute, and may even contain several non-equivalent segregation sites [10,14]. In such a case, one might question the accuracy of the approximation involving singly derived ΔG^0 value. The more general equations of our paper are essentially not related to the assumption of monolayer equivalent site segregation, and do not refer to concentration-independent ΔG^0 in dilute solid solutions, as do the L-H papers.

In conclusion, besides the latter remarks, the use of ideal solution in the strict sense (#1) as a reference system to excess thermodynamical quantities should not cause any confusion, since it is fully consistent with common basic definitions. While both approaches are legitimate, the different reference system (#3) employed by L-H is at the origin of the terminological disagreement. We hope that our paper together with this Reply to the Comment do contribute towards clarification of the terminological issues and the physical grounds of the relationship between the entropy and enthalpy of interfacial segregation.

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