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Comment on

"On the relationship between the entropy and enthalpy of interfacial segregation" by L. Rubinovich and M. Polak

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Abstract. The paper of L. Rubinovich and M. Polak [Eur. Phys. J. B **22**, 267 (2001)] contains some controversial items. The notation "excess" in connection with various thermodynamic quantities describing solute segregation on the basis of the Langmuir-McLean isotherm is used in a meaning contradictory to general thermodynamics. The approach used to interpret the linear relationship between segregation entropy and enthalpy results in rather strange conclusions. These items are discussed, and it is shown how a formulation with standard terms is in accordance with general thermodynamics.

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Recently, Rubinovich and Polak published a contribution to the presently discussed relationship between enthalpy and entropy of interfacial segregation [1]. Besides an original look at this correlation, their paper demonstrates an ambiguity which exists in the terminology of thermodynamic description of segregation and which is likely to result in confusion of the reader. The purpose of this comment is (i) to point out the difficulties that may arise with such an approach, and (ii) to elucidate other discrepancies of their work, and (iii) to enhance the basic understanding of segregation phenomena.

Although the term "excess" free energy of segregation is sometimes used in papers devoted to solute segregation, its use is not consistent with general thermodynamics. An example of such an incorrect application is demonstrated by Rubinovich and Polak in paper [1] as well as in their extended review [2]. The approach used by them is based on the idea that the *total change of Gibbs free energy due to segregation*, ΔG_I, that is equal to zero in equilibrium, can be decomposed into two parts, a configurational term and a remaining term [3]. In principle, this approach is correct, however, sometimes an inappropriate notation of these terms is used in the literature as demonstrated in references [1,2]: the configurational and the remaining terms are called *ideal*, ΔG_I^{id}, and *excess*, ΔG_I^{ex}, Gibbs free energy of segregation, respectively. Using this terminology, the Langmuir-McLean segregation isotherm can be expressed as

$$\frac{c_p}{1-c_p} = \frac{c}{1-c}\exp\left(-\frac{\Delta G_I^{ex}}{RT}\right), \tag{1}$$

where c_p and c are the atomic concentrations of element I at the interface Φ and in the bulk, respectively.

Accepting equation (1) in the presented form, the *excess* Gibbs free energy of segregation in is defined as the combination of standard chemical potentials of solute I and matrix element M at the interface and in the bulk (*cf.*, *e.g.*, [4]),

$$\Delta G_I^{ex} = \left(\mu_M^0 + \mu_I^{0,\Phi}\right) - \left(\mu_I^0 + \mu_M^{0,\Phi}\right). \tag{2}$$

Although the above derivation used by Rubinovich and Polak appears to be formally correct, it is based on a peculiar usage of the terms "excess" and "ideal", which are *different from their meaning in general thermodynamics.* As it is generally accepted in thermodynamics (*e.g.*, [5,6]), the term excess is exclusively dedicated to the *expression of differences between real and ideal behavior* while ΔG_I^{ex} used in equation (2) – as a combination of standard chemical potentials – is *principally ideal.* Therefore, this term

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should be called – in accordance with classical thermodynamics – *standard molar Gibbs free energy of segregation*, usually designed as ΔG_I^0. The designation excess (mainly in combination with the use of the term *ideal* in another sense) in this connection is incorrect from the viewpoint of classical thermodynamics and its usage in the description of segregation phenomena causes a considerable confusion. The reader cannot distinguish whether the authors consider the terms excess thermodynamic quantities as (1) the standard molar quantities of segregation as shown in equation (1) that are representative for segregation of a solute in infinitesimally diluted solid solution, or (2) the difference between real and ideal segregation behavior in concentrated and interacting systems that are of quite different nature and magnitude. In fact, the thermodynamically correct *excess Gibbs free energy of segregation*, can be expressed as a combination of activity coefficients γ of the segregant I and of the matrix element M both at an interface $\varPhi$ and in the bulk, $\Delta G_I^E = RT \ln\left[\gamma_I^{\varPhi}\gamma_M/\gamma_I\gamma_M^{\varPhi}\right]$. This term can be then correlated by a suitable approximation such as the Guttmann models of solute segregation in interacting multicomponent systems [7].

There are also some questionable parts in the discussion of the linear correlation between the standard molar entropy and enthalpy of segregation as it is presented in paper [1]. According to general thermodynamics, the standard molar free energy of segregation, ΔG_I^0 (ΔG_I^{ex}, as used in Ref. [1]), consists of two contributions, the standard molar enthalpy, ΔH_I^0, and the standard molar entropy, ΔS_I^0, $\Delta G_I^0 = \Delta H_I^0 - T\Delta S_I^0$, where T is the temperature. Recently, a close relationship between ΔH_I^0 and ΔS_I^0 was reported (*e.g.* [8]) and further described [9], that is given by

$$\Delta S_I^0 = \frac{\Delta H_I^0}{\tau} + \sigma. \tag{3}$$

The parameters τ and σ were interpreted as the characteristic temperature[1] and the entropy of segregation of element I at a boundary characterized by $\Delta H_I^0 = 0$, respectively [9]. In fact, ΔH_I^0 and ΔS_I^0 determine the interfacial composition in *infinitesimally diluted* (*non-interacting*) binary systems that fulfil equation (1). Combining equations (1) and (3) at the temperature $T = \tau$, we obtain $\Delta G_I^0(\tau) = -\sigma\tau$ and thus,

$$\sigma = R \ln\left[\left(\frac{c_p}{1-c_p}\right)_{T=\tau} \frac{1-c}{c}\right]. \tag{4}$$

Let us emphasise that this relation is *exclusively* valid for $T = \tau$. As ΔG_I^0 is independent of bulk concentration (Eq. (2)), the argument of the logarithmic term in equation (4) is constant [11].

Based on a rather complicated comparison of differences in the values of configurational entropy, $\Delta S^{id} = -R\ln\{[c_p(1-c)]/[(1-c_p)c]\}$, for different grain boundaries (*cf.* also Fig. 1 in Ref. [1]), Rubinovich and Polak obtained the same result. However, in their discussion of the temperature dependence of the "ideal configurational entropy" (*via* the temperature dependence of grain boundary concentration), the exclusive identity of the parameter σ and the "ideal configurational entropy" (*cf.* Eq. (4)) *at a characteristic temperature* τ is disappearing, although it is the principal condition here. The temperature τ is introduced as "some (although iso-concentration) temperature at which the anisotropy of ΔS_I^0 is much stronger than that of the configurational contribution" (cited from Ref. [1]). From this statement, it remains unclear how such a temperature can be defined. As shown in reference [12], this temperature is clearly defined as a temperature at which the values of the standard molar free energy of segregation are identical for a pair of grain boundaries. In fact, this temperature can vary for different pairs of interfaces but there exists an average value of τ that is used for the correlation expressed by equation (3). Rubinovich and Polak [1] further mention a concentration and temperature dependence of ΔS_I^0 and thus, suggest a possibility of concentration and temperature dependence of τ (itself a characteristic temperature) and σ. This statement is in contradiction with the definitions of standard molar enthalpy, entropy and free energy of segregation: Since they are defined as the respective thermodynamic quantities for impurity segregation in an *infinitesimally diluted solid solution*, ΔH_I^0, ΔS_I^0 and ΔG_I^0 do *principally not* depend on concentration.

To re-evaluate the values of τ and σ, Rubinovich and Polak [1] use equation (4) where the data on the solute concentration are determined as "the interfacial concentrations averaged over different tilt boundaries" (cited from Ref. [1]). Combination of equations (3) and (4) provides

$$-\sigma = R \ln\left[\left(\frac{X_I^{\varPhi}}{1-X_I^{\varPhi}}\right)_{T=\tau} \frac{1-X_I}{X_I}\right] = -\frac{\Delta H_I^0}{\tau} + \Delta S_I^0. \tag{5}$$

Therefore, "not surprisingly, the agreement between fitted and calculated values is good" (cited from Ref. [1]). Because the procedures for the determination of the parameters σ and τ in paper [8] on the one hand and in paper [1] on the other hand are identical, both should *principally* result in identical values. The small differences between fitted and calculated values of σ and τ result exclusively from the fact that these values were determined in reference [1] *via* averaging the interfacial concentrations, while they were obtained by averaging the values of ΔS_I^0 and ΔH_I^0 in reference [9]. As discussed in more detail in references [12,13], these differences arise from a wide anisotropy of the values of ΔH_I^0 and ΔS_I^0, and are controlled by the differences between arithmetic and geometric averages of these quantities.

In summary, the paper of Rubinovich and Polak [1] describes a rather peculiar approach to the interpretation of the linear dependence between segregation entropy and enthalpy. However, it is based on an inappropriate use of the term "excess" in the description of interfacial segregation that is not consistent with general thermodynamics. Moreover, a complicated discussion of the linear relation between segregation enthalpy and entropy results in

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[1] This term is sometimes called "compensation" temperature [10].

incorrect or trivial conclusions. They diminish the scientific value of this paper, and are unfortunately also contained in the otherwise excellent review paper of the same authors [2].

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