THERMODYNAMIC STATE FUNCTIONS OF INTERFACIAL SEGREGATION AND THEIR ROLE IN THE COMPENSATION EFFECT

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Received: December 20, 2008

Abstract. The physical meaning of thermodynamic state functions appearing in the Langmuir–McLean segregation isotherm – the standard Gibbs energy of segregation, the Gibbs energy of segregation, the excess Gibbs energy of segregation, and the effective Gibbs energy of segregation, and their enthalpy and entropy constituents – is elucidated. As an example, the importance of standard thermodynamic functions is demonstrated for the compensation effect.

1. INTRODUCTION
Interfacial segregation has been studied for a long time [1] because of its impact on various properties of materials, such as intergranular cohesion, creep-rupture life and catalytic properties [2]. Numerous papers on interfacial segregation offer a database on chemical composition of interfaces under specific conditions. Nevertheless, it is more important to disclose general trends that are capable to predict materials behavior under different thermal and structural conditions using appropriate thermodynamic relations [3,4]. However, some thermodynamic data published in literature are not clearly defined. It is obvious that their incorrect interpretation may substantially impede the understanding of fundamentals of interfacial segregation.

The aim of this paper is to characterize individual types of the thermodynamic state functions – Gibbs energy, enthalpy and entropy – used in the thermodynamic description of interfacial segregation, and to show the differences among them. Additionally, a suitable application of the fundamental thermodynamic functions – the standard enthalpy and entropy of interfacial segregation – is shown for example of the compensation effect.

2. LANGMUIR–MCLEAN TYPES OF SEGREGATION ISOTHERM
Characteristic changes of the thermodynamic state functions – Gibbs energy, G, enthalpy, H, and entropy, S – appear in the Langmuir–McLean types of the segregation isotherm (e.g. [4,5]). The segregation of a solute I at an interface Φ in a binary M–I system can be understood as an exchange of the components M and I between Φ and the volume [6]:

\[ M^* + I \Leftrightarrow M + I^*. \] (1)

The molar Gibbs energy of “reaction” (1), \( \Delta G \), is defined by the difference of the chemical potentials \( \mu_i \) of the right- and left-hand terms, and is equal to zero in equilibrium [6],

\[ \Delta G = \left( \mu_i^* + \mu_M \right) - \left( \mu_M^* + \mu_i \right) = 0. \] (2)

Here, \( \mu_i = \mu_i^{pure} + RT \ln a_i \), where \( \mu_i^{pure} \) is the standard chemical potential of pure i at temperature T and structure of M, \( a_i = \gamma_i X_i \) is the activity, \( \gamma_i \) is the activity coefficient, and \( X_i \) is the atomic fraction. Eq. (2) can be rewritten as
Fig. 1. Schematic representation of the Gibbs energy, $\Delta G_i$ (solid line) and the standard Gibbs energy, $\Delta G_i^0$ (dashed line) of grain boundary segregation in a binary system. (a) concentration dependence, (b) temperature dependence. An enrichment of the interface by the solute $I$ occurs at the bulk concentration $X_{i1}$ but the same interface is depleted by $I$ at $X_{i2}$. If $\Delta G_i = 0$, the interfacial concentration of $I$ is identical with its bulk concentration.

$$\frac{a_i^*}{a_i} = a_i \exp \left( -\frac{\Delta G_i^0}{RT} \right)$$  \hspace{1cm} (3)$$

with the standard molar Gibbs energy of segregation,

$$\Delta G_i^0 = \left( \mu_{i(m)}^0 + \mu_i^0 \right) - \left( \mu_{i(m)}^0 + \mu_i^0 \right).$$  \hspace{1cm} (4)$$

We can rewrite Eq. (3) as

$$\frac{X_i^*}{1 - X_i^*} = \frac{X_i}{1 - X_i} \exp \left( -\frac{\Delta G_i^0 + \Delta G_i^E}{RT} \right).$$  \hspace{1cm} (5)$$
using \( X_i = 1 - X \) for a binary system. In Eq. (5), the excess Gibbs energy of segregation, \( \Delta G^e \), represents a combination of the activity coefficients,

\[
\Delta G^e = \sum_{i=M} \Gamma_i = \sum_{i=M} \frac{m_i}{\Gamma_i} \ln \left( \frac{\gamma_i/\gamma_{iw}}{\gamma_i/\gamma_{iw}} \right)
\]

and thus, the difference between the segregation behavior of real and ideal systems. For simplicity, the molar Gibbs energy of interfacial segregation, \( \Delta G_i \), is defined as

\[
\Delta G_i = \Delta G^o + \Delta G^e.
\]

\( \Delta G \) consists of two terms, the standard contribution, \( \Delta G^o \), and the excess contribution, \( \Delta G^e \).

Eq. (5) represents the general form of the segregation isotherm. It was derived without any non-thermodynamic approximation, e.g. mutual interactions. This isotherm can be used for description of interfacial segregation in any system independently of its nature.

\( \Delta G_i \) (Eq. (7)) applied in Eq. (5) is frequently called “excess Gibbs energy of segregation”, \( \Delta G^e \) [7] or \( \Delta G^m \) [8]. It evokes very confusing terminological ambiguity connected with two excess terms with completely different meaning, \( \Delta G^e \) and \( \Delta G^r \).

Let us remind that since 1920s, the term “excess” is systematically applied to identify the deviations between real and ideal behavior [9]. The use of this term in context with interfacial properties was introduced much later [10]. In fact, the adjective “surface/interfacial excess” is unnecessary overdetermination because the term surface/interfacial itself already denotes the extra contribution of interfaces over bulk and therefore, it should not be used in this context [4].

3. PHYSICAL MEANING OF THE THERMODYNAMIC FUNCTIONS OF INTERFACIAL SEGREGATION

Due to terminological ambiguity, severe misunderstanding sometimes occurs in use of the thermodynamic functions of segregation. Let us characterize physical meaning of the types of thermodynamic functions, which can appear in segregation isotherm (5).

3.1. Thermodynamic functions of interfacial segregation, \( \Delta G_i, \Delta H_i \), and \( \Delta S_i \)

According to Eqs. (5) and (7), (molar) Gibbs energy of segregation, \( \Delta G_i \), completely determines the concentration, \( X_i^o \), of the solute I at the interface \( \Phi \), at given temperature \( T \) and bulk atomic fraction \( X_i \). \( \Delta G_i \) principally changes with changing concentrations \( X_i \) and \( X_i^o \), due to solute interaction (Fig. 1). The corresponding enthalpy, \( \Delta H_i \), and entropy, \( \Delta S_i \), of segregation, related to \( \Delta G_i \) according to \( G = H - TS \) [9], also depend on temperature and concentration (e.g. [7]). Therefore, these values can hardly be attributed to any general information, e.g. about the anisotropy of grain boundary segregation, because any orientation dependence of \( \Delta H_i \) and \( \Delta S_i \) varies in a complex way with temperature and composition [4].

3.2. Standard thermodynamic functions of interfacial segregation, \( \Delta G^o_i, \Delta H^o_i, \) and \( \Delta S^o_i \)

The standard (molar) Gibbs energy of interfacial segregation, \( \Delta G^o_i \), is defined by Eq. (2). It clearly follows from Eq. (2) that \( \Delta G^o_i \) (and consequently corresponding \( \Delta H^o_i \) and \( \Delta S^o_i \)) are principally independent of concentration (see Fig. 1a). \( \Delta G^o_i = \Delta G \) only for \( \gamma_i = 1 \), i.e. when \( \Delta G^e = 0 \) (Eqs. (5)–(7)). Despite this limitation, many systems behave practically ideal (e.g. [11,12]). Moreover, in an infinitesimally diluted (ideal) solid solution the amount of interfacial solute enrichment is very low and therefore, \( \Delta G^o_i \) characterizes the interfacial segregation of element I at a specific type of site of interface \( \Phi \) in the ideal system. The standard (molar) enthalpy, \( \Delta H^o_i \), and entropy, \( \Delta S^o_i \), of interfacial segregation are defined in analogy to \( \Delta G^o_i \) and have corresponding physical meaning. According to Eq. (3), \( \Delta G^o_i \) and thus \( \Delta H^o_i \) and \( \Delta S^o_i \), define the relation between the interface activities, \( a_i, \Phi \) and \( a_i, \Phi \), and the bulk activities, \( a_i, M \) and \( a_i, \), in the whole concentration range of a binary \( M-I \) system.

In analogy to Eq. (4), \( \Delta H^s_i \), \( \Delta S^s_i \) and molar specific heat of segregation, \( \Delta c_i^s \), are the respective combinations of the enthalpy, entropy and molar specific heats of the pure elements related to the interface and to the bulk. As \( c_i, \) is insensitive to presence of structural defects (\( \Delta c_r^s = 0 \), cf. [4]), \( \Delta H^s_i \) and \( \Delta S^s_i \) are independent of temperature. This independence is principal property of \( \Delta H^s_i \) and \( \Delta S^s_i \). The values of \( \Delta H^s_i \) and \( \Delta S^s_i \) change exclusively with the structure of the interface/site (i.e. with the energy of the interface/site) and with the nature of the solvent/solute. Therefore, \( \Delta H^s_i \) and \( \Delta S^s_i \) can be used for general purposes, for example, to characterize the principal anisotropy of interfacial segregation, which is directly related to the grain bound-
Fig. 2. Anisotropy of solute segregation at [100] symmetrical tilt grain boundaries in an Fe–3.55 at.%Si–0.00089at.%P–0.014at.%C alloy [3], represented by orientation dependence of different thermodynamic functions. (a) $\Delta G_p^0$ (empty symbols), $\Delta G_p$ (solid symbols), at 773K and 1173K. $\Delta G_{seg}^m$ (squares) represents the value of $\Delta G_p^0$ averaged over the same temperature range; (b) $\Delta G_{Si}^0$ (empty symbols) and $\Delta G_{Si}$ (solid symbols), at 773K ($\Delta G_{Si}^E$ is also indicated); (c) dependence of $\Delta H_{Si}^0$ on the misorientation angle $\theta^\circ[100]$. 
ary classification [4] as is demonstrated in Fig. 2. There, the orientation dependence of $\Delta G$ and $\Delta G^0$ is shown for phosphorus and silicon segregation at [100] symmetrical tilt grain boundaries in an Fe–Si–P–C base alloy [3]. While $\Delta G$ and $\Delta G^0$ for phosphorus are rather similar (Fig. 2a), they show a pronounced difference for silicon (Fig. 2b). A relatively high value of $\Delta G^0_\text{Si}$ (cf. Eq. (7) and Part C) is responsible for positive values of $\Delta G_{\text{Si}}$ for all grain boundaries at 773K suggesting depletion of the interfaces by silicon due to presence of other, more interfacially active elements (P,C) in the alloy [3]. However, $\Delta G_{\text{Si}}$ is negative in all cases indicating that silicon principally segregates at these interfaces in binary Fe–Si alloys [13]. As depicted in Fig. 2a, due to the small effect of $\Delta G^0_\text{Si}$ on segregation of phosphorus, the orientation dependence of both $\Delta G^0_\text{Si}$ and $\Delta G_\text{Si}$ is similar, showing local maxima for the 36.9°[100],[013], and 53.1°[100],[012] grain boundaries at 773K, but minima of $\Delta G^0_\text{P}$ and $\Delta G_\text{P}$ for these grain boundaries at 1173 K. At the latter temperature, minima of $\Delta G^0_\text{P}$ and $\Delta G_\text{P}$, were also observed at the 22.6°[100],[015] grain boundary (Fig. 2a). All these findings agree excellently with the orientation dependence of $\Delta H^0_\text{P}$ (cf. Fig. 2c), which characterizes the fundamental segregation tendencies of individual grain boundaries: The [015], [013], and [012] grain boundaries in α-iron are special with low tendency to solute segregation (singular maxima of $\Delta H^0_\text{P}$) [4]. $\Delta G_{\text{Si}}$ exhibits a minimum for the [012] but a maximum for the [013] interfaces while $\Delta G^0_{\text{Si}}$ shows maxima for both these special grain boundaries at 773K (Fig. 2b). This result clearly indicates that $\Delta G^0_\text{P}$ reflects the grain boundary classification while $\Delta G_\text{Si}$ does not.

### 3.3. Excess thermodynamic functions of interfacial segregation, $\Delta G^E$, $\Delta H^E$, and $\Delta S^E$

According to Eq. (7), the excess (molar) Gibbs energy of segregation, $\Delta G^E$, represents the difference between real and ideal behaviors with respect to interfacial segregation, $\Delta G^E = \Delta G^E - \Delta G^0$, and is exactly defined by the activity coefficients, $\gamma_i$ (Eq. (6)). Unfortunately, the information about the values of $\gamma_i$ of the involved components is usually unknown and hardly measurable. Therefore, this term is taken into account by simplified models, e.g. regular solid solution (Fowler) model for a binary system ($\Delta G^E = -2\alpha_\text{P} (X_\text{P}^0/X_\text{P})$) or Guttmann model for segregation in multicomponent systems ($\Delta G^E = -2\alpha_{ij} X_j^0 + \Sigma_{j k} \alpha_{ij} \alpha'_{jk} (X_j^0 - X_j)$), $\alpha_{ij}$ and $\alpha'_{ij}$, being the binary (Fowler) and the ternary interaction parameters, respectively [2].

The principal dependence of $\Delta G^0$, $\Delta G^E$, and $\Delta G_\text{Si}$ on concentration and temperature is schematically given in Fig. 1.

#### 3.4. Effective thermodynamic functions of interfacial segregation, $\Delta_{\text{seg}}^\text{eff}$, $\Delta H_{\text{seg}}^\text{eff}$, and $\Delta S_{\text{seg}}^\text{eff}$

Some published experimental data (and sometimes even theoretical work) are inconsistent with the above definitions. In general, these data are average values obtained by principally incorrect assumptions, e.g., by neglecting the spatial distribution of segregated species beneath the interface, averaging $\Delta G_\text{P}$ ($\Delta H_\text{P}$ or $\Delta S_\text{P}$) or $\Delta G^0_\text{P}$ for alloys of the same system but with different compositions, by averaging over a temperature range, or over various interfaces/sites (i.e. neglecting anisotropy) [4]. These data are called effective thermodynamic functions of segregation, which have no physical meaning [4,9]. $\Delta H_{\text{seg}}^\text{eff}$ and $\Delta S_{\text{seg}}^\text{eff}$ apparently possess similar properties as $\Delta H^0_\text{P}$ and $\Delta S^0_\text{P}$ – the concentration and temperature independence. Despite this artificial similarity, these two functions are principally different. Unfortunately, they are sometimes used in place of each other and therefore misinterpreted. Furthermore, it is sometimes argued that AES is only capable of providing values for $\Delta H_{\text{seg}}^\text{eff}$ and $\Delta S_{\text{seg}}^\text{eff}$ [9]. As pointed out in [4], in fact a correct quantification of AES results yields $\Delta H_\text{P}$ and $\Delta S_\text{P}$, which are the basis of derivation of $\Delta H^0_\text{P}$ and $\Delta S^0_\text{P}$ via the correction terms for $\Delta G^E$ as discussed in 3.3.

#### 4. Compensation Effect in Interfacial Segregation

One example of the obvious confusion in definition and application of thermodynamic functions is the compensation effect (CE). Generally, the CE is the linear dependence between characteristic enthalpy, $\Delta H^\text{CE}(\Psi)$, and entropy, $\Delta S^\text{CE}(\Psi)$, of a process or equilibrium state,

$$\Delta S^\text{CE}(\Psi) = \frac{\Delta H^\text{CE}(\Psi)}{T_{\text{ce}}} - \frac{\Delta G^\text{CE}(\Psi, T_{\text{ce}})}{T_{\text{ce}}},$$

where $\Delta H^\text{CE}(\Psi)$ and $\Delta S^\text{CE}(\Psi)$ change only with changing intensive thermodynamic variable(s) $\Psi$, such as magnetic field and interfacial energy also not temperature and pressure. $T_{\text{ce}}$ is the compensation temperature. $\Delta G^\text{CE}(\Psi, T_{\text{ce}})$ is the integration constant: In case of interfacial segregation it is...
Fig. 3. Relation between entropy and enthalpy of segregation of carbon at symmetrical tilt grain boundaries in $\alpha$-iron: (a) $\Delta S^0$ and $\Delta H^0$; (b) $\Delta S_\text{c}$ and $\Delta H_\text{c}$ at 923K; and (c) $\Delta H^\text{eff}$ and $\Delta S^\text{eff}$, representing the averages over the temperature range 773–1173K [4].
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Fig. 4. Relation between $\Delta S I^0$ and $\Delta H I^0$ for grain boundary segregation in $\alpha$-iron. Full symbols depict segregation of C (squares), P (triangles) and Si (circles) at individual grain boundaries, open symbols represent the data measured in polycrystalline $\alpha$-Fe ("average" grain boundaries) as found in literature. The upper and lower branches of the dependence represent the best fits of the data on solute segregation at interstitial sites and in substitution positions, respectively [14].

related to the characteristic configurational Gibbs energy of the system at $T_{ce}$ [4]. The CE has been detected for processes and states in various fields. Nevertheless, doubts about its existence are evoked mainly because of employment of inappropriate enthalpy–entropy pairs [4].

Let us elucidate this problem by a CE construction with different pairs of segregation enthalpy and entropy (Fig. 3). Fig. 3a shows a plot of $\Delta S C^0$ vs. $\Delta H C^0$ for segregation of carbon at well-characterised grain boundaries of $\alpha$-iron. It is evident that this plot exhibits a pronounced linear dependence between $\Delta S C^0$ and $\Delta H C^0$. On the other hand, no CE is observed for $\Delta S C$ and $\Delta H C$ at 923 K (Fig. 3b). This is because two contributions to segregation combine in $\Delta S C$ and $\Delta H C$. These two contributions are the tendency of carbon to segregate at grain boundaries of iron in infinitesimally diluted (ideal) solid solution, and the interaction of carbon with other segregating elements, phosphorus and silicon. In Fig. 3c, a plot of the physically meaningless values of $\Delta H C^0$ and $\Delta S C^0$ (i.e. $\Delta H C$ and $\Delta S C$ averaged over the temperature range 773–1173K) cannot be fitted with a linear relation, too. Fig. 3 clearly demonstrates that a necessary condition in establishing a linear dependence between the characteristic enthalpy and entropy is a single, well-defined mechanism of the considered process or state [4].

The range of existence of the CE (i.e. $T_{ce} = const$) for grain boundary segregation in $\alpha$-iron is quite large [4]. As is seen in Fig. 4, the linear dependence between $\Delta H I^0$ and $\Delta S I^0$ is very well fulfilled for carbon, phosphorus and silicon segregation at individual grain boundaries in $\alpha$-iron (solid symbols and lines) but also for other solutes segregating most probably at general interfaces, as measured in polycrystals [4,14,15]. The CE splits into two branches due to different mechanisms of grain boundary segregation – an upper branch for interstitial and a lower branch for substitutional sites [14]. The value of $T_{ce} = 930K$ is identical for both branches of the CE because $T_{ce}$ characterizes the matrix element [4]. Due to the wide range of existence, the CE can be used to predict values of $\Delta S I^0$. 
for many grain boundaries and many segregating elements [15].

Let us remind that the CE exists exclusively for a well-defined single process or state and is related to unambiguously defined state conditions. In grain boundary segregation, the only functions applicable for the CE are \( \Delta H^0 \) and \( \Delta S^0 \). When changing the intensive variables \( T \), the segregation mechanism must be conserved. Any overlapping process (e.g. solute interaction in segregation) has to be avoided because it may complicate the mechanism for which the CE is considered. This is the reason for principal excluding \( \Delta H^0 \) and \( \Delta S^0 \) as representatives of the CE.

5. CONCLUSIONS

A thorough analysis of the thermodynamic functions applicable to segregation isotherms of the Langmuir–McLean type disclosed that the standard functions of interfacial segregation, \( \Delta G^0, \Delta H^0, \) and \( \Delta S^0 \), are most fundamental and clearly defined. They characterize the general tendency of solute segregation at energetically most advantageous sites of the interface. The total functions of interfacial segregation, \( \Delta G, \Delta H, \) and \( \Delta S \), which are experimentally accessible, describe the true interfacial segregation in a system with a chosen bulk composition at a given temperature. It is shown that the excess functions of interfacial segregation, \( \Delta G^e, \Delta H^e, \) and \( \Delta S^e \), represent the difference between the above mentioned types of the respective functions. In contrast, the effective functions of interfacial segregation, \( \Delta G^w, \Delta H^w, \) and \( \Delta S^w \), given by average values for ranges of concentrations, orientations or temperatures, are physically meaningless. Application of different types of thermodynamic functions to the compensation effect demonstrate that the only functions in accordance with the required linear dependence between enthalpy and entropy of segregation are \( \Delta H^0 \) and \( \Delta S^0 \) owing to their unambiguous representation of a single state. An incorrect application of other enthalpy/entropy pairs must not be the reason for discarding any generalization or claiming the irrelevance of \( \Delta H^0 \) and \( \Delta S^0 \). Since many problems in mutual understanding arise from the use of the ambiguous term "excess", we recommend to use the adjective "excess" exclusively to describe the difference between real and ideal part of any thermodynamic function.

Acknowledgement

The support of the Czech Science Foundation (grant 202/06/0004) and the Academy of Sciences of the Czech Republic (grant KAN300100801) is gratefully acknowledged.

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