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

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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.

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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]:

$$M^{\Phi} + I \Leftrightarrow M + I^{\Phi}. \tag{1}$$

The molar Gibbs energy of "reaction" (1), ΔG, is defined by the difference of the chemical potentials μ_i of the right- and left-hand terms, and is equal to zero in equilibrium [6],

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

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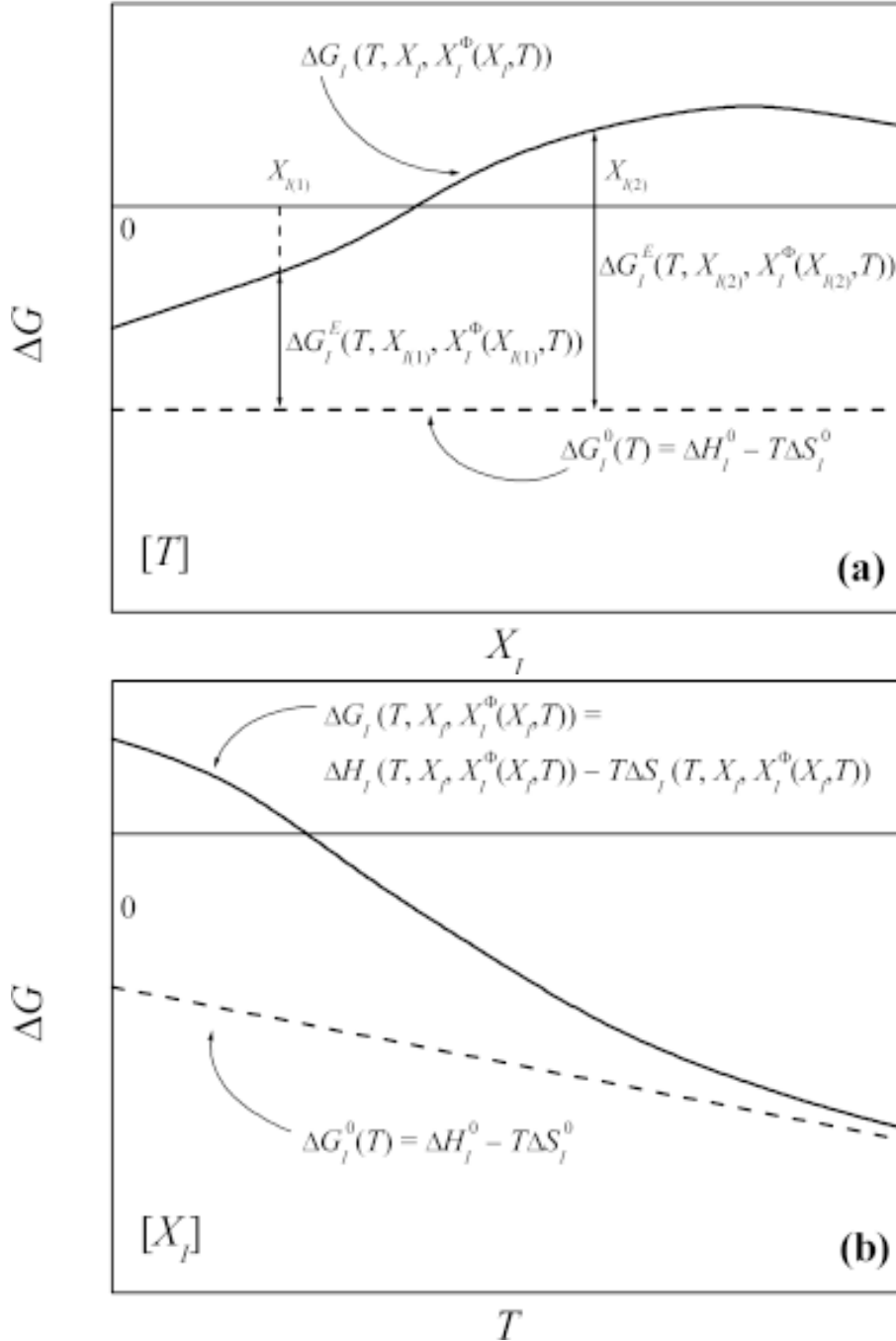
Fig. 1. Schematic representation of the Gibbs energy, ΔG_I (solid line) and the standard Gibbs energy, ΔG_I^0 (dashed line) of grain boundary segregation in a binary system. (a) concentration dependence, (b) temperature dependence. An enrichment of the interface by the solute I occurs at the bulk concentration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

$$\frac{a_I^\Phi}{a_M^\Phi} = \frac{a_I}{a_M} \exp\left(-\frac{\Delta G_I^0}{RT}\right) \tag{3}$$

with the *standard molar Gibbs energy of segregation,*

$$\Delta G_I^0 = \left(\mu_{I(M)}^{0,\Phi} + \mu_M^0\right) - \left(\mu_M^{0,\Phi} + \mu_{I(M)}^0\right). \tag{4}$$

We can rewrite Eq. (3) as

$$\frac{X_I^\Phi}{1-X_I^\Phi} = \frac{X_I}{1-X_I} \exp\left(-\frac{\Delta G_I^0 + \Delta G_I^E}{RT}\right). \tag{5}$$

using $X_M = 1 - X_I$ for a binary system. In Eq. (5), the *excess Gibbs energy of segregation, ΔG_I^E,* represents a combination of the activity coefficients,

$$\Delta G_I^E = \sum_{\substack{i=I,M; \\ bulk,\Phi}} \Delta \overline{G}_i^E = RT \ln \left(\frac{\gamma_I^\Phi \overline{\gamma}_M}{\gamma_I \gamma_M^\Phi} \right) \tag{6}$$

and thus, the difference between the segregation behavior of real and ideal systems. For simplicity, the *molar Gibbs energy of interfacial segregation,* ΔG_I, is defined as

$$\Delta G_I = \Delta G_I^0 + \Delta G_I^E. \tag{7}$$

ΔG_I consists of two terms, the standard contribution, ΔG_I^0, and the excess contribution, ΔG_I^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.

ΔG_I (Eq. (7)) applied in Eq. (5) is frequently called "excess Gibbs energy of segregation", ΔG^{xs} [7] or ΔG^{ex} [8]. It evokes very confusing terminological ambiguity connected with two *excess* terms with completely different meaning, ΔG_I^E and ΔG_I. 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 over-determination 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, ΔG_I, ΔH_I, and ΔS_I

According to Eqs. (5) and (7), *(molar) Gibbs energy of segregation, ΔG_I, completely determines*

the concentration, X_I^Φ, of the solute I at the interface Φ, at given temperature T and bulk atomic fraction X_I. ΔG_I principally changes with changing concentrations X_I and X_I^Φ, due to solute interaction (Fig. 1). The corresponding enthalpy, ΔH_I, and entropy, ΔS_I, of segregation, related to ΔG_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 ΔH_I and ΔS_I varies in a complex way with temperature and composition [4].

3.2. Standard thermodynamic functions of interfacial segregation, ΔG_I^0, ΔH_I^0, and ΔS_I^0

The *standard (molar) Gibbs energy of interfacial segregation, ΔG_I^0,* is defined by Eq. (2). It clearly follows from Eq. (2) that ΔG_I^0 (and consequently corresponding ΔH_I^0 and ΔS_I^0) are principally *independent of concentration* (see Fig. 1a). $\Delta G_I^0 \equiv \Delta G_I$ only for $\gamma_i \equiv 1$, i.e. when $\Delta G_I^E = 0$ (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, *ΔG_I^0 characterizes the interfacial segregation of element I at a specific type of sites of interface Φ in the ideal system.* The standard (molar) enthalpy, ΔH_I^0, and entropy, ΔS_I^0, of interfacial segregation are defined in analogy to ΔG_I^0 and have corresponding physical meaning. According to Eq. (3), ΔG_I^0 and thus ΔH_I^0 and ΔS_I^0, define the relation between the interface activities, $a_M \Phi$ and $a_I \Phi$, and the bulk activities, a_M, and a_I, in the whole concentration range of a binary *M–I* system.

In analogy to Eq. (4), ΔH_I^0, ΔS_I^0 and molar specific heat of segregation, Δc_p^0, 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_p, is insensitive to presence of structural defects ($\Delta c_p^0 = 0$, cf. [4]), ΔH_I^0 and ΔS_I^0 are *independent of temperature*. This independence is *principal property* of ΔH_I^0 and ΔS_I^0. The values of ΔH_I^0 and ΔS_I^0 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, ΔH_I^0 and ΔS_I^0 can be used for general purposes, for example, to characterize the principal anisotropy of interfacial segregation, which is directly related to the grain bound-
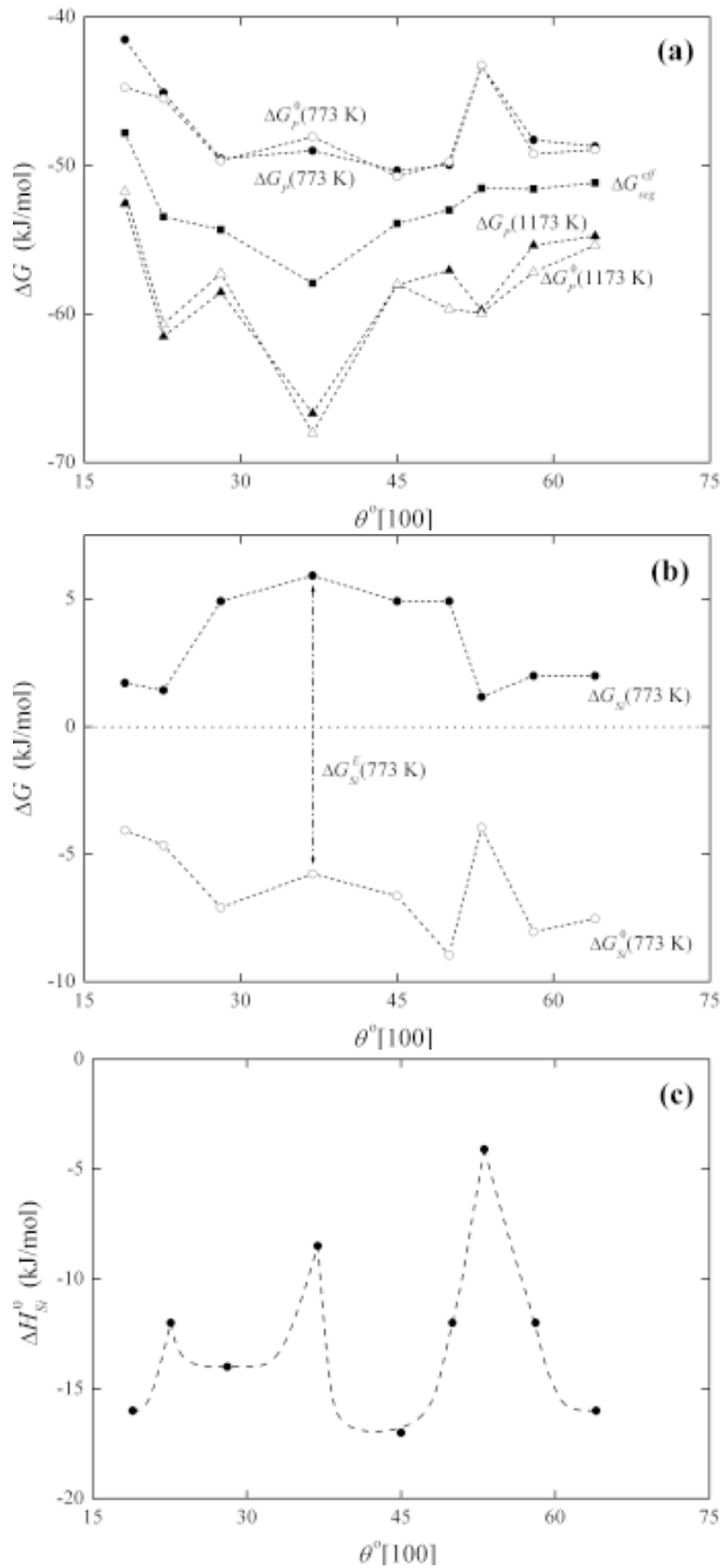
Fig. 2. Anisotropy of solute segregation at [100] symmetrical tilt grain boundaries in an Fe–3.55 at.%Si–00089at.%P–0.014at.%C alloy [3], represented by orientation dependence of different thermodynamic functions. (a) ΔG_P^0 (empty symbols), ΔG_P (solid symbols), at 773K and 1173K. ΔG_{seg}^{eff} (squares) represents the value of ΔG_P^0 averaged over the same temperature range; (b) ΔG_{Si}^0 (empty symbols) and ΔG_{Si} (solid symbols), at 773K (ΔG_{Si}^E is also indicated); (c) dependence of ΔH_{Si}^0 on the misorientation angle θ°[100].

ary classification [4] as is demonstrated in Fig. 2. There, the orientation dependence of ΔG_I and ΔG_I^0 is shown for phosphorus and silicon segregation at [100] symmetrical tilt grain boundaries in an Fe–Si–P–C base alloy [3]. While ΔG_I and ΔG_I^0 for phosphorus are rather similar (Fig. 2a), they show a pronounced difference for silicon (Fig. 2b). A relatively high value of ΔG_{Si}^E (cf. Eq. (7) and Part C) is responsible for positive values of ΔG_{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, ΔG_{Si}^0 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 ΔG_P^E on segregation of phosphorus, the orientation dependence of both ΔG_P^0 and ΔG_P is similar, showing local maxima for the 36.9°[100],{013}, and 53.1°[100],{012} grain boundaries at 773K, but minima of ΔG_P^0 and ΔG_P for these grain boundaries at 1173 K. At the latter temperature, minima of ΔG_P^0 and ΔG_P were also observed at the 22.6°[100],{015} grain boundary (Fig. 2a). All these findings agree excellently with the orientation dependence of ΔH_I^0 (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 ΔH_I^0) [4]. ΔG_{Si} exhibits a minimum for the {012} but a maximum for the {013} interfaces while ΔG_{Si}^0 shows maxima for both these special grain boundaries at 773K (Fig. 2b). This result clearly indicates that ΔG_I^0 reflects the grain boundary classification while ΔG_I does not.

3.3. *Excess* thermodynamic functions of interfacial segregation, ΔG_I^E, ΔH_I^E, and ΔS_I^E

According to Eq. (7), the *excess (molar) Gibbs energy of segregation*, ΔG_I^E, represents the *difference between real and ideal behaviors with respect to interfacial segregation*. $\Delta G_I^E = \Delta G_I^E - \Delta G_I^0$, and is exactly defined by the activity coefficients, γ_i, (Eq. (6)). Unfortunately, the information about the values of γ_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 ($\Delta G_I^E = -2\alpha_{IM}(X_I^\Phi/X_I^{0\Phi})$) or Guttmann model for segregation in multicomponent systems ($\Delta G_I^E = -2\alpha_{IM}X_I^\Phi + \Sigma_{J\neq I,M}\alpha'_{IJ}(X_I^\Phi - X_I)$, α_{IM}, and α'_{IJ} being the binary (Fowler) and the ternary interac-

tion parameters, respectively) [2]. The principal dependence of ΔG_I^0, ΔG_I^E, and ΔG_I on concentration and temperature is schematically given in Fig. 1.

3.4. *Effective* thermodynamic functions of interfacial segregation, ΔG_{seg}^{eff}, ΔH_{seg}^{eff}, and ΔS_{seg}^{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 ΔG_I (ΔH_I or ΔS_I) or ΔG_I^0 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]. ΔH_{seg}^{eff} and ΔS_{seg}^{eff} apparently possess similar properties as ΔH_I^0 and ΔS_I^0 – 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 ΔH_{seg}^{eff} and ΔS_{seg}^{eff} [9]. As pointed out in [4], in fact a correct quantification of AES results yields ΔH_I and ΔS_I, which are the basis of derivation of ΔH_I^0 and ΔS_I^0 via the correction terms for ΔG_I^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, $\Delta H^{ch}(\Psi_j)$, and entropy, $\Delta S^{ch}(\Psi_j)$, of a process or equilibrium state,

$$\Delta S^{ch}\left(\Psi_j\right) = \frac{\Delta H^{ch}\left(\Psi_j\right)}{T_{ce}} - \frac{\Delta G^{ch}\left(\Psi_j, T_{ce}\right)}{T_{ce}}, \qquad (8)$$

where $\Delta H^{ch}(\Psi_j)$ and $\Delta S^{ch}(\Psi_j)$ change only with changing intensive thermodynamic variable(s) Ψ_j such as magnetic field and interfacial energy albeit not temperature and pressure. T_{ce} is the compensation temperature. $\Delta G^{ch}(\Psi_j, T_{ce})$ is the integration constant: In case of interfacial segregation it is
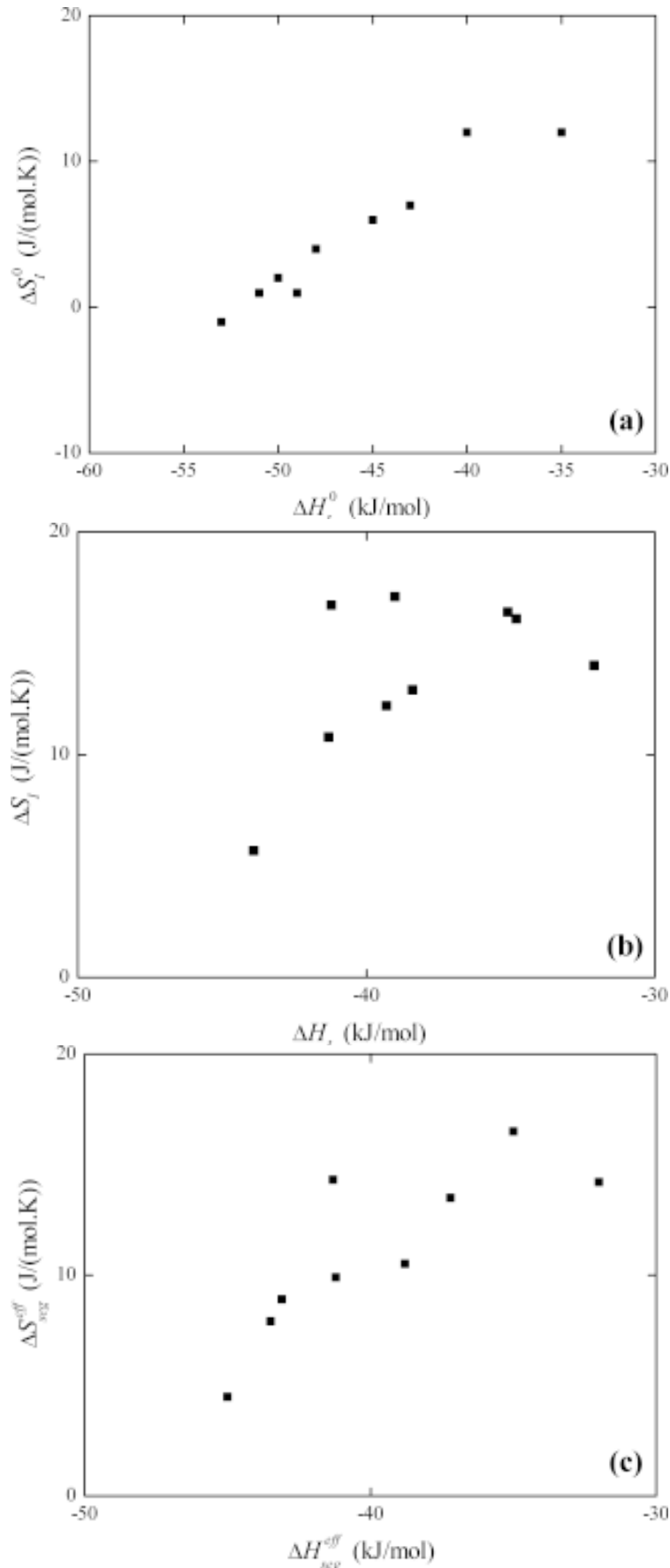
Fig. 3. Relation between entropy and enthalpy of segregation of carbon at symmetrical tilt grain boundaries in α-iron: (a) ΔS_C^0 and ΔH_C^0; (b) ΔS_C and ΔH_C, at 923K; and (c) ΔH_C^{eff} and ΔS_C^{eff}, representing the averages over the temperature range 773–1173K [4].
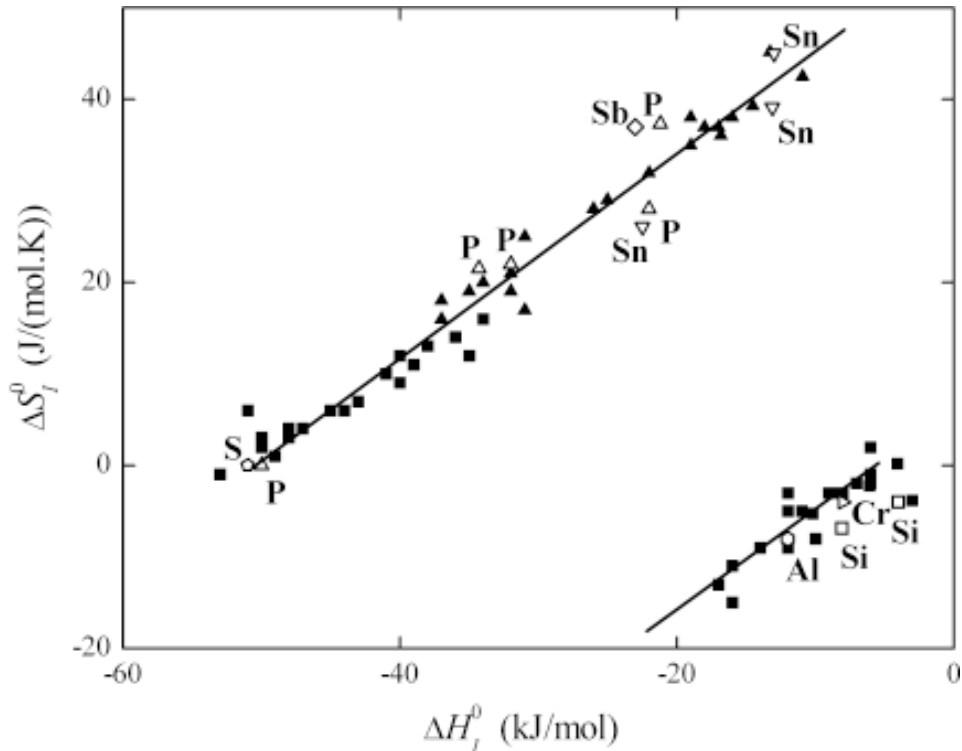
Fig. 4. Relation between ΔS_I^0 and ΔH_I^0 for grain boundary segregation in α-iron. Full symbols depict segregation of C (squares), P (triangles) and Si (circles) at individual grain boundaries, open symbols represent the data measured in polycrystalline α-Fe ("average" grain boundaries) as found in 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 ΔS_C^0 vs. ΔH_C^0 for segregation of carbon at well-characterised grain boundaries of α-iron. It is evident that this plot exhibits a pronounced linear dependence between ΔS_C^0 and ΔH_C^0. On the other hand, no *CE* is observed for ΔS_C and ΔH_C at 923 K (Fig. 3b). This is because two contributions to segregation combine in ΔS_C and ΔH_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 ΔH_C^{eff} and ΔS_C^{eff} (i.e. ΔH_C and ΔS_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 a-iron is quite large [4]. As is seen in Fig. 4, the linear dependence between ΔH_I^0 and ΔS_I^0 is very well fulfilled for carbon, phosphorus and silicon segregation at individual grain boundaries in a-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 ΔS_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 ΔH_I^0 and ΔS_I^0. When changing the intensive variables Ψ_j, 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 ΔH_I and ΔS_I 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*, ΔG_I^0, ΔH_I^0, and ΔS_I^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*, ΔG_I, ΔH_I, and ΔS_I, 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*, ΔG_I^E, ΔH_I^E, and ΔS_I^E, represent the difference between the above mentioned types of the respective functions. In contrast, the *effective functions of interfacial segregation*, ΔG_{seg}^{eff}, ΔH_{seg}^{eff}, ΔS_{seg}^{eff}, 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 ΔH_I^0 and ΔS_I^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 ΔH_I^0 and ΔS_I^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

References

[1] *Interfacial Segregation*, ed. by W.C. Johnson and J.M. Blakely (ASM: Metals Park (OH), 1979).

[2] E.D. Hondros, M.P. Seah, S. Hofmann and P. Lejček, In: *Physical Metallurgy,* ed. by R.W. Cahn and P. Haasen (4th ed., North–Holland, Amsterdam, 1996), p. 1201.

[3] P. Lejček and S. Hofmann // *Crit. Rev. Sol. State Mater. Sci.* **20** (1995) 1.

[4] P. Lejček and S. Hofmann // *Crit. Rev. Sol. State Mater. Sci.* **33** (2008) 133.

[5] D. McLean, *Grain Boundaries in Metals* (Clarendon, Oxford, 1957).

[6] J. DuPlessis // *Sol. State Phenom.* **11** (1990) 1.

[7] P. Wynblatt and D. Chatain // *Metall. Mater. Trans. A* **37** (2006) 2595.

[8] M. Polak and L. Rubinovich // *Surface Sci. Rep.* **38** (2000) 127.

[9] G.N. Lewis and M. Randall, *Thermodynamics* (McGraw–Hill, New York, 1923).

[10] J.W. Cahn, In: *Interfacial Segregation*, ed. by W.C. Johnson and J.M. Blakely (ASM, Metals Park (OH), 1979), p. 3.

[11] H. Erhart and H.J. Grabke // *Met. Sci.* **15** (1981) 401.

[12] J. Janovec, D. Grman, J. Perháčová, P. Lejček, J. Patscheider and P. Ševc // *Surf. Interface Anal.* **30** (2000) 354.

[13] P. Lejček // *Prog. Surf. Sci.* **35** (1991) 209.

[14] P. Lejček and S. Hofmann, In: *Encyclopedia of Materials: Science and Technology – Updates*, ed. by K.H.J. Bunshaw, R.W. Cahn, M.C. Flemings, E.J. Kramer and S. Mahajan (Pergamon, Amsterdam, 2002), #200115.

[15] P. Lejček, S. Hofmann and J. Janovec // *Mater. Sci. Eng. A* **462** (2007) 76.