On the concentration dependence of the surface tension of liquid metallic alloys
Theoretical basis

[1]G.Kaptay, fkmkap@gold.uni-miskolc.hu
[2]Z.Papp zoltanp@dai.ed.ac.uk

[1]Professor at the Department of Physical Chemistry of the University of Miskolc
3515 Hungary, Miskolc, Egyetemvaros

[2]Student at University of Edinburgh, Division of informatics
Scotland, UK

Abstract

In the present paper a revised version of Butler equation is derived to calculate the surface tension in multi-component liquid metallic solutions. The effects of surface active complexes (intermetallic compounds) in liquid metallic solutions is also discussed.

1. Introduction

Surface tension is one of the basic thermodynamic properties of liquid metallic alloys, determining their behavior in different technological processes. Surface tension is determined by usual parameters of state – temperature and composition. Although there are very few experimental results on the concentration dependence of the surface tension of multi-component alloys, for complex modeling of different materials technologies this information is obviously needed. Therefore there is a need for a model, by which the surface tension of multi-component metallic alloys can be related to bulk thermodynamic properties. Such a model can serve as a basis for an 'interfacial module' in complex thermodynamic softwares.

In the present paper such a model will be derived from basic thermodynamic principles, and compared to the existing models in the literature. First, let us consider the models given in the literature so far, and then, let us derive our own equation.

2. Models presented in the literature

The surface tension of multi-component solutions is traditionally interpreted in terms of the Gibbs adsorption isotherms. For practical use, however, the method developed by Butler (based on Gibbs) is much more 'user-friendly' [1]. According to Butler, the (partial) surface tension of component i in a multi-component solution can be written as:

$$\sigma_i = \sigma_i^o + \frac{R \cdot T}{\omega_i} \cdot \ln \frac{a_i^*}{a_i} \tag{1}$$

where σ_i^o – is the surface tension of pure component i at the same temperature and pressure,
R – gas constant,
T – absolute temperature,
ω_i – partial molar surface area of component i,
a_i and $a_i{}^*$ - the activity of component i in the bulk and in the surface phase of the
solution, respectively.

The surface phase will be in equilibrium, if all the components will have the same partial surface tension values, i.e. if the following equality is fulfilled between components i and j:

$$\sigma_i = \sigma_j \tag{2}$$

For an n-component solution $(n-1)$ equalities such as Eq.(2) should be fulfilled. If the composition of the bulk solution is given, from those $(n-1)$ equations the surface composition can be obtained, as it is characterized by $(n-1)$ independent variables. For performing such a procedure, the following thermodynamic values are needed:

i.   the surface tension of pure components as function of temperature,
ii.   the activities in the bulk phase, expressed through its composition and T,
iii.   the activities in the surface phase, expressed through its composition and T,
iv.   the partial molar surface area values expressed through the surface composition and T.

From the above list of initial parameters one can see that the new information needed for the evaluation of the concentration dependence of the surface tension is ω_i and a_i^*. Instead of activity, usually the activity coefficient of component i in the surface is expressed, defined as $\gamma_i^* = a_i^*/x_i^*$. These values are usually expressed in the literature using the following approximations [2-10]:

$$\omega_i = f \cdot V_i^{2/3} \cdot N_{Av}^{1/3} \tag{3}$$

$$\ln \gamma_i^* = \beta \cdot \ln \gamma_i \tag{4}$$

where **f** – is the geometrical factor, usually used as 1.091 (taken equal to the value derived for the (111) plane of solid fcc crystals),
V_i – the partial molar volume of component i in the solution (for simplicity usually taken equal to the molar volume of pure component i),
N_{Av} – the Avogadro number,
β - a semi-empirical parameter, usually defined as the ratio of the broken bonds at the surface.

In different models parameter β is taken equal to different values for describing the surface tension of liquid metallic solutions. Hoar and Melford [2] used a value between $\beta = 0.5$ and 0.667 to describe Sn-Pb and Pb-In systems. Monma and Sudo [3] applied a coefficient between $\beta = 0.80$ and 0.84 for Cu-Ni and Ni-Mo systems. Speiser at al. [4-5] applied $\beta = 0.75$ to describe Fe-Cu, Cu-Pb, Sn-Pb, Ag-Pb, Pb-In, Bi-Ag, Cu-Al, Fe-Si and Ni-Si systems. The same coefficients of $\beta = 0.75$ was used by Lee et al [6] for the Fe-Ni system. Tanaka et al. studied the influence of parameter β in the interval between 0.5 and 1 on the final results for Ag-Pb, Cu-Pb, Sn-Pb, Cu-Fe, Cu-Al, Ni-Si and various Fe-alloys [7]. In the later paper of Tanaka et al [8] the semi-empirical coefficient $\beta = 0.83$ was suggested from the analysis of the dependency of the surface tension of pure liquid metals on their enthalpy of evaporation, and this coefficient was applied to the Cu-Pn and Fe-Si systems. The coefficient of $\beta = 0.83$ suggested by Tanaka et al [8] was successfully applied by Moser et al. to describe the Ag-Sn [9] and the Pb-Sn [10] systems.

3. The model developed in the present paper

In our model the Butler concept (Eq-s 1-2) will be used as a basis, but it will be altered by considering separately the enthalpy and the entropy parts. Eq.(3) also remains valid, but the value of coefficient f will be altered. The theory will be re-constructed from the very beginning, starting with the model for the surface tension of one-component liquid metals.

3.1. The surface tension of one-component liquid metals

By definition, the partial excess surface Gibbs energy of component i in the pure phase i can be obtained as the difference between the Gibbs energy of the surface and bulk phases:

$$\sigma_i^o \cdot \omega_i^o = \Delta_f G_i^{*o} - \Delta_f G_i^o = (\Delta_f H_i^{*o} - \Delta_f H_i^o) - T \cdot (S_i^{*o} - S_i^o) \tag{5}$$

The molar surface area of pure component i can be written in an analogous way with Eq.(3):

$$\omega_i^o = f \cdot \left(V_i^o\right)^{2/3} \cdot N_{Av}^{1/3} \tag{6}$$

The enthalpy and entropy differences between the surface and bulk phases in pure liquid metals can be written as:

$$\Delta_f H_i^{*o} - \Delta_f H_i^o = (1 - \beta) \cdot (-\Delta_c H_i^o) \tag{7}$$

$$S_i^{*o} - S_i^o = R \cdot \ln \frac{V_i^{*0}}{V_i^o} \tag{8}$$

where $\Delta_c H_i^o$ – is the cohesion enthalpy of a pure liquid metal, being approximately equal to the condensation enthalpy (for a more advanced definition see [11]),

$\beta = z*/z$, the ratio of the coordination numbers in the surface and bulk phases,
V_i^{*o} and V_i^o are the molar volumes of pure component i in the surface and bulk phases, respectively.

According to our previous works [12-13], pure liquid metals have a surface structure close to the (111) plane of the fcc crystal, i.e. $z* = 9$. Combining this value with the average coordination number in pure liquid metals ($z \cong 11$), $\beta \cong 9/11 = 0.818$. From the same surface model the value of parameter f in Eq.(6): $f \cong 1.06$ [12-13]. The entropy difference in Eq.(8) approximately equals +4 J/molK [12-13]. The combination of these theoretically established parameters provide a perfect match with the experimentally determined surface tension values of pure liquid metals [12-13]. Let us mention, that these values are close to those applied by Tanaka et al [8] ($\beta = 0.83, f = 1.091$, entropy contribution neglected).

Substituting Eq-s (6-8) into Eq.(5) the final expression for the surface tension of pure component i can be written as:

$$\sigma_i^o = \frac{(1 - \beta) \cdot (-\Delta_c H_i^o) - R \cdot T \cdot \ln \dfrac{V_i^{*o}}{V_i^o}}{f \cdot (V_i^o)^{2/3} \cdot N_{Av}^{1/3}} \tag{9}$$

3.2. The partial surface tension of component *i* in the multi-component liquid metallic solution

For a partial surface tension of component *i* in the multi-component liquid solution Eq.(5) can be re-written, but with omitting the subscript ^{o}, referring to the pure phase:

$$\sigma_i \cdot \omega_i = \Delta_f G_i^* - \Delta_f G_i = (\Delta_f H_i^* - \Delta_f H_i) - T \cdot (S_i^* - S_i) \tag{10}$$

The partial molar surface area of component *i* can be written by Eq.(3). However, we take $f = 1.06$, being equal to the value of f derived for the pure liquid metal, and being independent of concentration. The partial molar volume is defined as:

$$V_i = V_i^o + \Delta V_i^E(x_i^*) \tag{11}$$

where ΔV_i^E is the excess partial molar volume of component i, having the concentration dependence valid for the bulk phase, but being a function of the composition of the surface phase.

The enthalpy difference is composed of that in the pure phase, taking into account the partial mixing enthalpy terms *(ΔH_i)*. The partial mixing enthalpy of the surface phase is a function of the surface composition, and is reduced by coefficient *β*, to take into account the reduced coordination number at the surface:

$$\Delta_f H_i^* - \Delta_f H_i = (1-\beta) \cdot (-\Delta_c H_i^o) + \beta \cdot \Delta H_i(x_i^*) - \Delta H_i(x_i) \tag{12}$$

The entropy term will include the term given above for the pure phase, the configurational entropy term and the partial excess mixing entropy term. Non of these quantities should be multiplied by a correction factor of *β* (or any other coefficient), at least, in the first approximation:

$$S_i^* - S_i = R \cdot \ln \frac{V_i^{*0}}{V_i^o} + R \cdot \ln \frac{x_i}{x_i^*} + \Delta S_i^E(x_i^*) - \Delta S_i^E(x_i) \tag{13}$$

Substituting Eq-s (11-13) into Eq.(10), and taking into account Eq.(9), the following final result is obtained:

$$\sigma_i = \sigma_i^o \cdot \left(1 + \frac{\Delta V_i^E(x_i^*)}{V_i^o}\right)^{2/3} + $$
$$+ \frac{R \cdot T \cdot \ln x_i^* + \beta \cdot \Delta H_i(x_i^*) - T \cdot \Delta S_i^E(x_i^*) - R \cdot T \cdot \ln x_i - \Delta H_i(x_i) + T \cdot \Delta S_i^E(x_i)}{f \cdot (V_i^o + \Delta V_i^E(x_i^*))^{2/3} \cdot N_{Av}^{1/3}} \tag{14}$$

Re-arranging Eq.(14) to be alike the Butler equation:

$$\sigma_i = \sigma_i^o \cdot \left(1 + \frac{\Delta V_i^E(x_i^*)}{V_i^o}\right)^{2/3} + \frac{R \cdot T}{\omega_i} \cdot \ln \frac{a_i^*}{a_i} \tag{15}$$

with the definition of γ_i^*:

$$R \cdot T \cdot \ln \gamma_i^* = \beta \cdot \Delta H_i(x_i^*) - T \cdot \Delta S_i^E(x_i^*) \qquad (16)$$

One can see that Eq-s (15-16) are different from Eq-s (1, 4). If Eq-s (15-16) are combined with Eq.(2), the concentration dependence of surface tension can be calculated, supposing that the surface tension and molar volume of pure components are known as function of temperature, and all the excess functions $(\Delta H_i, \; \Delta S_i^E, \; \Delta V_i^E)$ are known as function of composition of the bulk liquid metal and temperature. Generally, no analytical solution exists for this problem, and thus usually numerical methods are applied (see [14]).

The analytical solution can be found only for the binary ideal solution A-B, if the two components have the same molar volume. Then, the composition of the surface phase and the surface tension can be calculated as:

$$x_A^* = \frac{x_A}{k \cdot (1 - x_A) + x_A} \qquad (17.a)$$

$$\sigma = \sigma_A^o - \frac{R \cdot T}{\omega} \cdot \ln\left[k \cdot (1 - x_A) + x_A\right] \qquad (17.b)$$

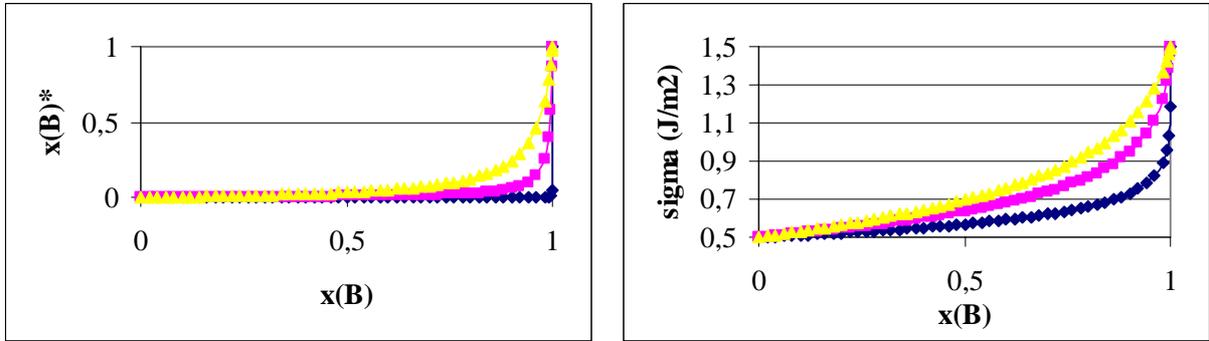$$k = \exp\left[(\sigma_A^o - \sigma_B^o) \cdot \frac{\omega}{R \cdot T}\right] \qquad (17.c)$$

Fig.1. The concentration dependence of the surface composition (left) and surface tension (right) of the binary ideal solution $(\sigma_A^o = 0.5$ J/m^2, $\sigma_B^o = 1.5$ J/m^2, $V_A^o = V_B^o = 10^{-4}$ m^3/mol) (curves from bottom to top correspond to 500 K, 1,000 K and 1,500 K)

The concentration dependence of the surface composition and the surface tension of a binary ideal solution are given in Fig 1. One can see that even in an ideal solution there is a great tendency to segregation of a component with a less surface tension value (component A) to the surface phase, leading to a very non-linear concentration dependence of the surface tension. As one can see from Fig.1, this tendency decreases with temperature, as at higher temperature the role of bulk configurational entropy is increased.

4. On the role of intermetallic compounds on the concentration dependence of σ

As is obvious from phase diagrams, in many metallic phases intermetallic compounds can form. Some of those compounds melt congruently, and thus obviously remain stable even in a liquid state, especially, if there is a significant non-metallic bond exists between the components. Such systems are often described in the literature using the 'associated solution model' [15-18]. If there is a significant part of ionic bonding in the intermetallic compound, its own surface tension is usually below the surface tensions of its constituent pure metals [12]. In these cases, minimum points on the concentration dependence of the surface tension are expected. However, no minimum points can be described by the formalism given above.

In order to describe mathematically the systems with associates, an associate solution model should first be applied. Then, in the binary system, at least three quasi-components (the two monomers and at least one associate) will exist. The concentration dependence of such a system can be described only, if the surface tension of the pure liquid intermetallic is known, and the system is treated as a 3-component system. For this first the equilibrium bulk concentrations of the three components should be found from bulk thermodynamic values (see [15-18]). If the surface tension of the liquid intermetallic is not known, it can be estimated by a fitting procedure, using experimental data.

Conclusions

The Butler equation has been revised in the present paper to describe more correctly the concentration dependence in multi-component liquid metals. Calculations are performed in [14]. The hypothesis is given about the possible role of intermetallic compounds on the minimum points observed on the concentration – surface tension curves. Numerical calculations will be performed in the future to prove this hypothesis.

Literature

1. Butler J.A.V.: Proc.Roy.Soc., A135 (1932) 348-375
2. Hoar T.P., Melford D.A., Trans. Faraday Soc. 53 (1957) 315-326
3. Monma K., Sudo H., J.Japan Inst. Metals, 25 (1961) 68-68 and 143-147
4. Speiser R., Poirier D.R., Yeum K., Scripta Metall., 21 (1987) 687-692
5. Yeum K., Speiser R., Poirier D.R., Metall. Trans. B., 20 B (1987) 693-703
6. Lee H.K., Frohberg M.G., Hajra J.P., Steel research, 64 (1993) 191-196
7. Tanaka T., Iida T., Steel research, 65 (1994) 21-28
8. Tanaka T., Hack K., Iida T., Hara S., Z.Metallkunde, 87 (1996) 380-389
9. Moser Z., Gasior W., Pstrus J, J. of Phase Equilibria, 22 (2001) 254-258
10. Gasior W., Moser Z., Pstrus J., J. of Phase Equilibria, 22 (2001) 20-25
11. G.Kaptay, G.Csicsovszki, M.S.Yaghmaee, Materials' World (e-journal, accessible at: http://materialworld.fw.hu), July, 2001.
12. G.Kaptay: Thesis for dr. habil, University of Miskolc, 1998, 51 pp.
13. G.Kaptay, E.Báder, L.Bolyán, Materials Science Forum, vols. 329-330 (2000) 151-156.
14. Z.Papp, G.Kaptay – see this volume
15. K.Wasai, K.Mukai, J. Japan Inst. of Metals, 46 (1982) 266-274
16. F.Sommer, Z. Metallkunde, 73 (1982) 72-76 and 77-86
17. G.Kaptay, E.Berecz, Chemical Papers, 45 (1991) 145-158
18. M.S.Yaghmaee, G.Kaptay, G.Jánosfy, Materials Science Forum, 329-330 (2000) 519-524.