Relationship between surface tension and Gibbs energy, and application of Constrained Gibbs Energy Minimization

Youn-Bae Kang

Graduate Institute of Ferrous Technology, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea

A B S T R A C T

In the context of a boundary phase model, surface tension (σ) of a solution can be regarded as a system property of an equilibrium between a bulk phase and a surface phase. In the present article, a geometric relationship is shown among molar Gibbs energy of the bulk phase (g), that of the surface phase (g^s), and corresponding surface tension of the system. The geometric relationship is based on a phase equilibrium between the bulk phase and the surface phase, under a constraint: constant surface area (A). The relationship is consistent with the proposal of Butler, Proc. R. Soc. Lond. A: Math. Phys. Eng. Sci., 135 (1932) 348 [1], and is mathematically equivalent to the Constrained Gibbs Energy Minimization (CGEM) for the surface tension calculation by Pajarre et al., Calphad 30 (2006) 196 [7]. The geometric relationship can be simply utilized by available CALPHAD type code, in order to calculate surface tension of a solution composed of any number of components. Role of various properties (surface tension (σ_i^o) and molar surface area (A_i^o) of pure components, excess Gibbs energy of the bulk phase and that of the surface phase) in the surface tension and surface concentration is examined using the CGEM.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

In the theoretical calculation of surface tension, one of widely applied concepts is that a surface of a condensed material may be considered as a thin separated phase, so to speak, a surface phase. An assumption is made that the surface phase is supposed to be in equilibrium with a corresponding bulk phase. As a result, constitution of the surface phase may be known, and the surface tension of the bulk phase may be derived. This approach has been widely used in order to calculate surface tension of liquid alloys, mostly utilizing the proposal of Butler [1] and subsequent several modifications [2–6]. While this approach is, in principle, valid generally in multicomponent system, many of previous researches utilizing this approach have been limited to binary systems because of complexity for solving equations. A new approach has been proposed by Pajarre et al. [7] where the surface tension can be calculated in a simple manner utilizing commercially available CALPHAD type code [8], even in multicomponent system. However, although mathematical aspect of the surface tension calculation was given, the principle for the calculation of surface tension is to be more explicitly described in the view of thermodynamic equilibrium.

In the present article, it is shown that how the CALPHAD approach, which has generally been used to calculate phase diagram and thermodynamic properties of multicomponent–multiphase system, can be utilized in the calculation of surface tension as well as the surface constitution (surface concentration). In this regard, a relationship between the surface tension and the Gibbs energy of solution is first described for a binary system. The binary system is treated as a pseudo-ternary system taking into account a new system component, "area". A graphical representation is provided in order for better understanding the relationship. Based on this relationship, a series of phase equilbria are calculated using the CALPHAD code, and surface tension and surface concentration are obtained as the results of the phase equilibrium calculations. With the aid of such simple method, surface tension and surface concentration of binary systems of various conditions are predicted. Role of various properties including surface tension, molar surface area of pure components, excess Gibbs energy in bulk and in surface phases is discussed. Finally, results of example calculations are shown for a ternary system and a quaternary system, not only for the surface tension, but also for the surface concentration.

2. Surface tension calculation

According the Butler [1], a surface of a solution is considered as a separate phase, distinguished from the corresponding bulk phase. Moreover, the surface phase is assumed to be confined to a monolayer of atoms. In the following, superscript ^{s} refers to "surface", throughout the present article.

E-mail address: ybkang@postech.ac.kr

Nomenclature

σ	surface tension of a solution, $N\,m^{-1}$
σ_i°	surface tension of a pure component i, $N\,m^{-1}$
A	surface area, m^2
A_i°	molar surface area of a pure component i, $m^2\,mol^{-1}$
a_i^s	activity of a component i in the surface phase, –
A_i	partial surface area of a component i, $m^2\,mol^{-1}$
a_i	activity of a component i in the bulk phase, –
G	Gibbs energy of the bulk phase, J
G^{sys}	Gibbs energy of the whole system ($=G+G^s$), J
G^s	Gibbs energy of the surface phase, J
g_i^s	partial Gibbs energy of a component i in the surface phase, $J\,mol^{-1}$
g_i	partial Gibbs energy or chemical potential of a

	component i, $J\,mol^{-1}$
g_i°	molar Gibbs energy of a pure component i, $J\,mol^{-1}$
$g_i^{s,\circ}$	molar Gibbs energy of a pure component i in a surface phase, $J\,mol^{-1}$
$g_{X(i)}$	partial Gibbs energy or chemical potential of X in a i–X system when the bulk i and the surface i are in equilibrium, $J\,mol^{-1}$
n_i^s	number of moles of a component i in the surface phase, mol
n_i	number of moles of a component i in the bulk phase, mol
V_i	(partial) molar volume of component i, $m^3\,mol^{-1}$
X_i^s	concentration of a component i in the surface phase, –
X_i	concentration of a component i in the bulk phase, –

2.1. Butler model

Let us consider a binary A–B system, and the system is composed of the bulk and the surface (s) phases. They are in thermodynamic equilibrium:

$$G^{sys} = G + G^s \tag{1}$$

$$G^{sys} = \left(n_A g_A + n_B g_B\right) + \left(n_A^s g_A + n_B^s g_B + A\sigma\right) \tag{2}$$

where G^{sys}, G, and G^s are the Gibbs energy of the whole system, that of the bulk phase, and that of the surface phase, respectively. n_i, n_i^s, and g_i are number of moles of a component i in the bulk phase, that in the surface phase, and partial Gibbs energy of a component i, respectively. A and σ are surface area and surface tension of the solution, respectively.

In the above equation, G^s contains two contributions, a chemical contribution ($n_A^s g_A + n_B^s g_B$) and a physical contribution ($A\sigma$). Using the following constraint,

$$A = n_A^s A_A + n_B^s A_B \tag{3}$$

where A_i is a partial area of the component i, the total Gibbs energy of the system becomes

$$G^{sys} = \left(n_A g_A + n_B g_B\right) + n_A^s\left(g_A + A_A\sigma\right) + n_B^s\left(g_B + A_B\sigma\right) \tag{4}$$

Let us define a partial Gibbs energy of A in the surface phase [9]:

$$g_A^s \equiv g_A + A_A\sigma = g_A^{s,\circ} + RT\ln a_A^s \tag{5}$$

which has two contributions: chemical contribution g_A and physical contribution $A_A\sigma$. It may be regarded that the partial Gibbs energy of A in the surface phase is *shifted* from that in the bulk phase as much as $A_A\sigma$. And the activity of A in the surface phase (a_A^s) is defined along with the standard molar Gibbs energy of A in the surface phase ($g_A^{s,\circ}$).

At equilibrium, g_A(bulk, chemical)$=g_A$(surface, chemical). Therefore,

$$g_A = g_A^\circ + RT\ln a_A \quad \text{(bulk)} \tag{6}$$

$$g_A = g_A^s - A_A\sigma \quad \text{(surface)} \tag{7}$$

$$g_A = g_A^{s,\circ} + RT\ln a_A^s - A_A\sigma \quad \text{(surface)} \tag{8}$$

When $X_A = 1$ in both phases, $a_A = a_A^s = 1$, $A_A = A_A^\circ$, and $\sigma = \sigma_A^\circ$:

$$g_A^{s,\circ} = g_A^\circ + A_A^\circ\sigma_A^\circ \tag{9}$$

Eq. (9) may be seen as a *change of reference state* of A in the surface

phase. Therefore, the chemical contribution to the partial Gibbs energy in the surface becomes

$$g_A = g_A^\circ + A_A^\circ\sigma_A^\circ + RT\ln a_A^s - A_A\sigma \tag{10}$$

By comparing Eqs. (6) and (10),

$$A_A^\circ\sigma_A^\circ - A_A\sigma = RT\ln\frac{a_A}{a_A^s} \tag{11}$$

and

$$\sigma = \sigma_A^\circ\frac{A_A^\circ}{A_A} + \frac{RT}{A_A}\ln\frac{a_A^s}{a_A} \tag{12}$$

If A_A is assumed to be the same as the A_A°, the Butler equation for the surface tension is obtained [1,7]:

$$\sigma = \sigma_A^\circ + \frac{RT}{A_A^\circ}\ln\frac{a_A^s}{a_A} \tag{13}$$

Similar equation is also obtained for B:

$$\sigma = \sigma_B^\circ + \frac{RT}{A_B^\circ}\ln\frac{a_B^s}{a_B} \tag{14}$$

The molar surface area of the components, for example A_A, is generally estimated from the corresponding molar volume:

$$A_A = L\left(N_{Av}\right)^{1/3}V_A^{2/3} \tag{15}$$

where L is usually assumed to be 1.091 for liquid metals of closed packed structures [3]. N_{Av} is the Avogadro's number. The A_A is a function of composition (X_A). However, as information of the A_A for liquid solution is usually not known, it has been assumed to be the molar surface area of pure component A, A_A°.

In order to calculate the surface tension in the binary A–B system, there are two equations (Eqs. (13) and (14)) and two unknowns (σ and concentration of B (or A) in the surface phase, X_B^s), for given T, P, and X_B.

By subtracting the two equations,

$$\frac{\sigma_A^\circ - \sigma_B^\circ}{RT} = \frac{1}{A_B^\circ}\ln\frac{a_B^s}{a_B} - \frac{1}{A_A^\circ}\ln\frac{a_A^s}{a_A} \tag{16}$$

and solving Eq. (16), the surface concentration X_B^s (and subsequently X_A^s) can be obtained. Back substitution of the X_B^s in Eq. (14) yields the σ.

In an n-component system, there are n equations similar to Eqs. (13) and (14). Also, there are n unknowns (σ, X_i^s where $i = 2...n$). Simultaneously solving these n non-linear equations requires a sort of numerical approaches such as Newton–Raphson method.