

Extension of the Gibbs–Duhem Equation to the Partial Molar Surface Thermodynamic Properties of Solutions

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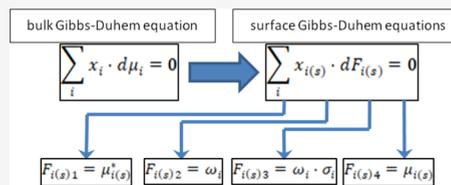
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ABSTRACT: In this paper, the Gibbs–Duhem equation is extended to the partial molar surface thermodynamic properties of solutions. According to the surface Gibbs–Duhem equations, the sum of the mole fractions of the components in the surface region of a bulk solution multiplied by different partial molar surface quantities should equal zero if summation is taken by all components of the solution. There are four different partial molar surface quantities identified in this paper for which the surface Gibbs–Duhem equation is proven to be valid: (i) the reduced surface chemical potential, (ii) the surface chemical potential, (iii) the partial molar surface area, and (iv) the partial molar excess surface Gibbs energy = the product of partial molar surface area and the partial surface tension. The first one is known since Guggenheim (1940), but the other three are presented here for the first time. It is also demonstrated here how to apply the surface Gibbs–Duhem equations: (i) it is proven that the model equation applied by us recently for the reduced chemical potential [*Adv Coll Interf Sci* 2020, 283, 102212] obeys one of the surface Gibbs–Duhem equations, (ii) in contrary, it is proven that the model equation suggested by us recently for the partial molar surface area contradicts one of the surface Gibbs–Duhem equations; therefore, a new (and simpler) model equation for the partial molar surface areas of the components is suggested here that obeys the surface Gibbs–Duhem equation. It is also shown that the Butler equation obeys one of the surface Gibbs–Duhem equations. It is also concluded that surface composition in equilibrium should be one that ensures minimum surface tension.



1. INTRODUCTION

The Gibbs–Duhem equation^{1–3} is a well-known and very useful equation for the partial molar thermodynamic quantities of bulk solutions.^{4–9} There are many models to extend the bulk thermodynamic properties to surface thermodynamic properties.^{10–35} Guggenheim¹¹ was the first to show that the Gibbs–Duhem equation can be extended to one of the partial molar surface quantities (see also refs 12, 15, 17, 23, 24). In this paper, the Gibbs–Duhem equation is extended even further: it is shown here to be valid for three further partial molar surface quantities.

2. METHODS

2.1. Gibbs–Duhem Equation Derived for Bulk Partial Molar Quantities of Solutions. Let us consider a homogeneous bulk solution phase with different components denoted as *i*. The total amount of matter (*n*, mol) in this bulk phase is written as

$$n = \sum_i n_i \quad (1a)$$

where *n_i* (mol) is the amount of matter of component *i* in the bulk phase. Now, let us define the mole fraction (denoted as *x_i*, dimensionless) of component *i* in this bulk solution as

$$x_i \equiv \frac{n_i}{n} \quad (1b)$$

The fundamental Gibbs equation written at constant pressure and constant temperature for the integral Gibbs energy of a bulk solution phase (*G*, *J*)¹ is shown as

$$dG = \sum_i \mu_i \cdot dn_i \quad (1c)$$

where *μ_i* (J/mol) is the chemical potential (equal to the partial molar Gibbs energy) of component *i* in the bulk solution phase. The integral form of eq 1c can be written as

$$G = \sum_i n_i \cdot \mu_i \quad (1d)$$

Now, let us take the full differential of eq 1d:

$$dG = \sum_i n_i \cdot d\mu_i + \sum_i \mu_i \cdot dn_i \quad (1e)$$

Note that eq 1e is the full differential of eq 1d, but eq 1c is not. Now, let us make the *dG* values equal in eqs 1c and 1e. From here, the following equation is obtained:

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$$\sum_i n_i \cdot d\mu_i = 0 \quad (1f)$$

Dividing each term of eq 1f by the total amount of matter in the given solution phase and taking into account eq 1b, the following equation is obtained:

$$\sum_i x_i \cdot d\mu_i = 0 \quad (1g)$$

Equation 1g is the well-known Gibbs–Duhem equation. In eq 1g, μ_i can be replaced by other bulk molar partial quantities, such as $U_{m,i}$, $H_{m,i}$, $S_{m,i}$, $V_{m,i}$, $C_{p,m,i}$, etc. (or sometimes denoted as u_i , h_i , s_i , v_i , $c_{p,i}$, etc.). Now, let us write a simplified version of eq 1g for a two-component A–B system as

$$(1 - x_B) \cdot \frac{d\mu_A}{dx_B} + x_B \cdot \frac{d\mu_B}{dx_B} = 0 \quad (1h)$$

where the materials balance equation ($x_A + x_B = 1$) was also applied. The integral molar Gibbs energy of the bulk phase (defined as $G_m \equiv G/n$, J/mol) for the two-component regular solution is written here as an example

$$G_m = (1 - x_B) \cdot G_{m,A}^o + x_B \cdot G_{m,B}^o + R \cdot T \cdot [(1 - x_B) \cdot \ln(1 - x_B) + x_B \cdot \ln x_B] + L \cdot x_B \cdot (1 - x_B) \quad (1i)$$

where $G_{m,A}^o$ (J/mol) is the standard molar Gibbs energy of the pure component A, $G_{m,B}^o$ (J/mol) is the same for pure component B, $R = 8.3145$ J/mol K is the universal gas constant, T (K) is the absolute temperature, and L (J/mol) is the bulk molar interaction energy between components A and B (the components attract each other at $L < 0$, repel each other at $L > 0$, and are neutral to each other at $L = 0$; the latter case is called the “ideal solution”). The chemical potentials of the components can be calculated as

$$\mu_A = G_m - x_B \cdot \frac{dG_m}{dx_B} \quad (1j)$$

$$\mu_B = G_m + (1 - x_B) \cdot \frac{dG_m}{dx_B} \quad (1k)$$

The derivative of G_m by x_B using eq 1i is

$$\frac{dG_m}{dx_B} = G_{m,B}^o - G_{m,A}^o + R \cdot T \cdot \ln\left(\frac{x_B}{1 - x_B}\right) + L \cdot (1 - 2 \cdot x_B) \quad (1l)$$

Substituting eqs 1i and 1l into eqs 1j and 1k,

$$\mu_A = G_{m,A}^o + R \cdot T \cdot \ln(1 - x_B) + L \cdot x_B^2 \quad (1m)$$

$$\mu_B = G_{m,B}^o + R \cdot T \cdot \ln x_B + L \cdot (1 - x_B)^2 \quad (1n)$$

The derivatives of eqs 1m and 1n by x_B are

$$\frac{d\mu_A}{dx_B} = -\frac{R \cdot T}{1 - x_B} + 2 \cdot L \cdot x_B \quad (1o)$$

$$\frac{d\mu_B}{dx_B} = \frac{R \cdot T}{x_B} - 2 \cdot L \cdot (1 - x_B) \quad (1p)$$

Now, let us substitute eqs 1o and 1p into eq 1h:

$$(1 - x_B) \cdot \left(-\frac{R \cdot T}{1 - x_B} + 2 \cdot L \cdot x_B\right) + x_B \cdot \left[\frac{R \cdot T}{x_B} - 2 \cdot L \cdot (1 - x_B)\right] = 0 \quad (1q)$$

After some rearrangements of eq 1q, $0 = 0$ is obtained. This means that the regular solution model of eq 1i obeys the Gibbs–Duhem equation, and so it is one of the thermodynamically meaningful solutions models. The same conclusion follows when the last term of eq 1i is extended to the Redlich–Kister polynomial^{36–38}

$$G_m = (1 - x_B) \cdot G_{m,A}^o + x_B \cdot G_{m,B}^o + R \cdot T \cdot [(1 - x_B) \cdot \ln(1 - x_B) + x_B \cdot \ln x_B] + [L_0 + L_1 \cdot (1 - 2 \cdot x_B) + L_2 \cdot (1 - 2 \cdot x_B)^2 + \dots] \quad (1r)$$

where L_j (J/mol) is the interaction energy between the components of the j th order ($j = 0, 1, 2$, etc.). However, let us also note that not all mathematical forms obey the Gibbs–Duhem equation. Consider for example the simplistic model equation being the same as eq 1i but without the last part $(1 - x_B)$ of its last term. Repeating the same procedure as above for this simplistic model equation, one can find that the Gibbs–Duhem equation is not obeyed. Thus, this simplistic model equation is not an appropriate model for a solution.

The above example demonstrates the usefulness of the Gibbs–Duhem equation in proving or disproving the validity of different thermodynamic model equations for bulk solutions. The surface Gibbs–Duhem equations to be derived below will be useful in a similar way to select proper model equations for the partial molar surface properties of solutions.

3. RESULTS AND DISCUSSION

3.1. Derivation of the First Surface Gibbs–Duhem Equation. Let us consider a surface region of a homogeneous bulk phase with different components denoted as i . The total amount of matter in the surface region (n_s , mol) is written as

$$n_s = \sum_i n_{i(s)} \quad (2a)$$

where $n_{i(s)}$ (mol) is the amount of matter of component i in the surface region of the bulk phase. Now, let us define the surface mole fraction (denoted as $x_{i(s)}$, dimensionless) of component i in the surface region of this phase as

$$x_{i(s)} \equiv \frac{n_{i(s)}}{n_s} \quad (2b)$$

The second fundamental Gibbs equation written at constant pressure, constant temperature, and constant bulk composition for the surface integral Gibbs energy of this phase (G_s , J) is

$$dG_s = \sum_i \mu_{i(s)} \cdot dn_{i(s)} + \sigma \cdot dA \quad (2c)$$

where $\mu_{i(s)}$ (J/mol) is the surface chemical potential (equal to the surface partial molar Gibbs energy) of component i in the surface region of the bulk phase, σ (J/m²) is the surface tension of the phase, and A (m²) is the surface area of the phase. Let us note that starting from this point, all dY_i values are understood as $dY_i/dx_{B(s)}$ (see eqs 2o, 3d, and 6e) and not as dY_i/dx_B , the latter being valid only above for the bulk Gibbs–Duhem equation (see eq 1h). The integral form of eq 2c can be written as

$$G_s = \sum_i n_{i(s)} \cdot \mu_{i(s)} + \sigma \cdot A \quad (2d)$$

Now, let us take the full differential of eq 2d:

$$dG_s = \sum_i n_{i(s)} \cdot d\mu_{i(s)} + \sum_i \mu_{i(s)} \cdot dn_{i(s)} + \sigma \cdot dA + A \cdot d\sigma \quad (2e)$$

Note that eq 2e is the full differential of eq 2d, but eq 2c is not. Now, let us make eqs 2c and 2e equal: from here, the following equation is obtained:

$$\sum_i n_{i(s)} \cdot d\mu_{i(s)} + A \cdot d\sigma = 0 \quad (2f)$$

Let us define the integral molar surface area of a phase (ω , m²/mol) being the surface area covered by 1 mol of atoms (molecules) in the surface layer^{22,28,35,39,40}

$$\omega \equiv \left(\frac{dA}{dn_s} \right)_{p,T,n} \quad (2g)$$

The integral form of eq 2g is

$$A = \omega \cdot n_s \quad (2h)$$

Any integral quantity can be written as the weighted average of its partials

$$\omega = \sum_i x_{i(s)} \cdot \omega_i \quad (2i)$$

where ω_i (m²/mol) is the partial molar surface area of component i , being the surface area covered by the same component along the surface and is defined as^{22,28,35,39,40}

$$\omega_i \equiv \left(\frac{dA}{dn_{i(s)}} \right)_{p,T,n,n_{j \neq i(s)}} \quad (2j)$$

Dividing each term of eq 2f by the total amount of matter in the surface region of the phase (n_s) and taking into account eqs 2b and 2h, the following equation is obtained:

$$\sum_i x_{i(s)} \cdot d\mu_{i(s)} + \omega \cdot d\sigma = 0 \quad (2k)$$

Substituting eq 2i into eq 2k, the final equation is obtained after some rearrangements:

$$\sum_i x_{i(s)} \cdot (d\mu_{i(s)} + \omega_i \cdot d\sigma) = 0 \quad (2l)$$

Equation 2l is the first surface Gibbs–Duhem equation derived in this paper. The same equation was also derived by Guggenheim¹¹ (see also refs 12, 15, 17, 24). The simplest way to prove the validity of eq 2l is to remind that it follows from the same eq 2f, from which the widely accepted Gibbs adsorption equation follows.²² Note that the expression in the parentheses of eq 2l is the differential form of the reduced surface chemical potential of component i in the surface region of the solution, defined as²⁸

$$\mu_{i(s)}^* \equiv \mu_{i(s)} + \omega_i \cdot \sigma \quad (2m)$$

Substituting eq 2m into eq 2l, the first surface Gibbs–Duhem equation written for the reduced surface chemical potential follows in its shortest form as

$$\sum_i x_{i(s)} \cdot d\mu_{i(s)}^* = 0 \quad (2n)$$

For a binary A–B solution, eq 2n is written similarly to eq 1h:

$$(1 - x_{B(s)}) \cdot \frac{d\mu_{A(s)}^*}{dx_{B(s)}} + x_{B(s)} \cdot \frac{d\mu_{B(s)}^*}{dx_{B(s)}} = 0 \quad (2o)$$

Now, let us apply the first surface Gibbs–Duhem equation to check whether the following model equations suggested previously²⁸ for the reduced chemical potentials obey it or not:

$$\mu_{A(s)}^* = \mu_{A(s)}^{*o} + R \cdot T \cdot \ln(1 - x_{B(s)}) + k \cdot L \cdot x_{B(s)}^2 \quad (2p)$$

$$\mu_{B(s)}^* = \mu_{B(s)}^{*o} + R \cdot T \cdot \ln x_{B(s)} + k \cdot L \cdot (1 - x_{B(s)})^2 \quad (2q)$$

where $\mu_{A(s)}^{*o}$ (J/mol) is the standard reduced surface chemical potential of component A, $\mu_{B(s)}^{*o}$ (J/mol) is the same for component B, and k (dimensionless) is the ratio of surface to bulk coordination numbers.²⁸ Now, let us write the derivatives of eqs 2p and 2q by $x_{B(s)}$:

$$\frac{d\mu_{A(s)}^*}{dx_{B(s)}} = -\frac{R \cdot T}{1 - x_{B(s)}} + 2 \cdot k \cdot L \cdot x_{B(s)} \quad (2r)$$

$$\frac{d\mu_{B(s)}^*}{dx_{B(s)}} = \frac{R \cdot T}{x_{B(s)}} - 2 \cdot k \cdot L \cdot (1 - x_{B(s)}) \quad (2s)$$

Now, let us substitute eqs 2r and 2s into eq 2o:

$$(1 - x_{B(s)}) \cdot \left[-\frac{R \cdot T}{1 - x_{B(s)}} + 2 \cdot k \cdot L \cdot x_{B(s)} \right] + x_{B(s)} \cdot \left[\frac{R \cdot T}{x_{B(s)}} - 2 \cdot k \cdot L \cdot (1 - x_{B(s)}) \right] = 0 \quad (2t)$$

After some rearrangements, eq 2t simplifies to 0 = 0. Thus, eqs 2p and 2q obey the first surface Gibbs–Duhem equation. This proves that eqs 2p and 2q are proper model equations for the reduced surface chemical potentials. It is an important result as eqs 2p and 2q were used to derive the second Butler equations, while the first Butler equation is written as^{10,16,21,22,25,28}

$$\sigma = \sigma_A = \sigma_B \quad (2u)$$

where σ_A (J/m²) is the partial surface tension of component A, while σ_B (J/m²) is the partial surface tension of component B, defined in ref 16 and written by the second Butler equations^{10,21,22,25,28}

$$\sigma_A = \sigma_A^o \cdot \frac{\omega_A^o}{\omega_A} + \frac{R \cdot T}{\omega_A} \cdot \ln \frac{1 - x_{B(s)}}{1 - x_B} + \frac{L}{\omega_A} \cdot (k \cdot x_{B(s)}^2 - x_B^2) \quad (2v)$$

$$\sigma_B = \sigma_B^o \cdot \frac{\omega_B^o}{\omega_B} + \frac{R \cdot T}{\omega_B} \cdot \ln \frac{x_{B(s)}}{x_B} + \frac{L}{\omega_B} \cdot [k \cdot (1 - x_{B(s)})^2 - (1 - x_B)^2] \quad (2w)$$

where σ_A^o (J/m²) is the surface tension of pure A, σ_B^o (J/m²) is the same for pure B, ω_A^o (J/m²) is the molar surface area of pure component A, and ω_B^o (J/m²) is the same for pure component B. Let us note that eqs 2v and 2w are written in agreement with the model eqs 1m, 1n, 2p, and 2q.

As follows from the above, the following three equations are in agreement with each other: (i) the Gibbs adsorption equation, (ii) the Butler equations, and (iii) the first surface Gibbs–Duhem equation. The mutual agreement of these three equations means that any of the above three equations can be derived as a combination of another two above equations.

3.2. Derivation of the Second Surface Gibbs–Duhem Equation. Now, let us take the full differential of eq 2m and let us substitute the resulting equation into eq 2n:

$$\sum_i x_{i(s)} \cdot (d\mu_{i(s)} + \sigma \cdot d\omega_i + \omega_i \cdot d\sigma) = 0 \quad (3a)$$

Taking into account eq 2l, eq 3a is simplified as

$$\sum_i x_{i(s)} \cdot \sigma \cdot d\omega_i = 0 \quad (3b)$$

Now, let us divide both sides of eq 3b by σ :

$$\sum_i x_{i(s)} \cdot d\omega_i = 0 \quad (3c)$$

Equation 3c is the second surface Gibbs–Duhem equation, valid for the partial molar surface areas of the components. For a two-component A–B solution, it is written similarly to eq 2o:

$$(1 - x_{B(s)}) \cdot \frac{d\omega_A}{dx_{B(s)}} + x_{B(s)} \cdot \frac{d\omega_B}{dx_{B(s)}} = 0 \quad (3d)$$

Now, let us apply the second Gibbs–Duhem equation to check whether the commonly used model equations,²⁸ written as follows, are valid or not:

$$\omega_i = f \cdot N_{Av}^{1/3} \cdot V_{m,i}^{2/3} \quad (4a)$$

where f (dimensionless) is a geometrical parameter,²⁸ $N_{Av} = 6.02 \times 10^{23}$ 1/mol is the Avogadro number, and $V_{m,i}$ (m^3/mol) is the partial molar volume of component i . Let us apply a regular solution model for the partial molar volumes, similar to eqs 1m and 1n:

$$V_{m,A} = V_{m,A}^o + L_V \cdot x_{B(s)}^2 \quad (4b)$$

$$V_{m,B} = V_{m,B}^o + L_V \cdot (1 - x_{B(s)})^2 \quad (4c)$$

where $V_{m,A}^o$ (m^3/mol) is the standard molar volume of component A, $V_{m,B}^o$ (m^3/mol) is that for component B, and L_V (m^3/mol) is the interaction volume. Now, let us substitute eqs 4b and 4c into eq 4a:

$$\omega_A = f \cdot N_{Av}^{1/3} \cdot [V_{m,A}^o + L_V \cdot x_{B(s)}^2]^{2/3} \quad (4d)$$

$$\omega_B = f \cdot N_{Av}^{1/3} \cdot [V_{m,B}^o + L_V \cdot (1 - x_{B(s)})^2]^{2/3} \quad (4e)$$

Now, let us take the derivatives of eqs 4d and 4e by $x_{B(s)}$:

$$\frac{d\omega_A}{dx_{B(s)}} = \frac{4}{3} \cdot f \cdot L_V \cdot x_{B(s)} \cdot \left(\frac{N_{Av}}{V_{m,A}} \right)^{1/3} \quad (4f)$$

$$\frac{d\omega_B}{dx_{B(s)}} = -\frac{4}{3} \cdot f \cdot L_V \cdot (1 - x_{B(s)}) \cdot \left(\frac{N_{Av}}{V_{m,B}} \right)^{1/3} \quad (4g)$$

Now, let us substitute eqs 4f and 4g into eq 3d:

$$\frac{4}{3} \cdot f \cdot L_V \cdot N_{Av}^{1/3} \cdot x_{B(s)} \cdot (1 - x_{B(s)}) \cdot (V_{m,A}^{-1/3} - V_{m,B}^{-1/3}) = 0 \quad (4h)$$

At any $L_V \neq 0$ and $x_{B(s)} \neq 0$ or $x_{B(s)} \neq 1$ (i.e., for any real solution), eq 4h is valid only if $V_{m,A} = V_{m,B}$. However, the latter condition is generally not valid, so the second surface Gibbs–Duhem equation is not obeyed for partial molar surface areas modeled by eqs 4d and 4e. This means that eqs 4d and 4e are not proper equations to model the partial molar surface areas. Now, let us introduce some simpler model equations for the partial molar surface areas, being analogues to eqs 4b and 4c:

$$\omega_A = \omega_A^o + L_\omega \cdot x_{B(s)}^2 \quad (5a)$$

$$\omega_B = \omega_B^o + L_\omega \cdot (1 - x_{B(s)})^2 \quad (5b)$$

where L_ω (m^2/mol) is the interaction surface area. Substituting eqs 5a and 5b into eq 2i, a new equation for the integral molar surface area is obtained as

$$\omega = (1 - x_{B(s)}) \cdot \omega_A^o + x_{B(s)} \cdot \omega_B^o + x_{B(s)} \cdot (1 - x_{B(s)}) \cdot L_\omega \quad (5c)$$

where the suggested model equations for the three model parameters are taken in agreement with eq 4a as

$$\omega_i^o = f \cdot N_{Av}^{1/3} \cdot (V_{m,i}^o)^{2/3} \quad (5d)$$

$$L_\omega = f \cdot N_{Av}^{1/3} \cdot L_V^{2/3} \quad (5e)$$

Now, let us take the derivatives of eqs 5a and 5b by $x_{B(s)}$:

$$\frac{d\omega_A}{dx_{B(s)}} = 2 \cdot L_\omega \cdot x_{B(s)} \quad (5f)$$

$$\frac{d\omega_B}{dx_{B(s)}} = -2 \cdot L_\omega \cdot (1 - x_{B(s)}) \quad (5g)$$

Now, let us substitute eqs 5f and 5g into eq 3d:

$$2 \cdot L_\omega \cdot (1 - x_{B(s)}) \cdot x_{B(s)} \cdot (1 - 1) = 0 \quad (5h)$$

As follows from eq 5h, the second surface Gibbs–Duhem equation is valid (as $1 - 1 = 0$) for the partial molar surface areas modeled by eqs 5a and 5b. In other words, using our new, second surface Gibbs–Duhem equation, we were able to correct the previously suggested wrong model equations for the partial molar surface areas. The new model eqs 5a and 5b provide a way to improve the Butler eqs 2v and 2w.

3.3. Derivation of the Third Surface Gibbs–Duhem Equation. Now, let us extend the first surface Gibbs–Duhem eq 2n by a second term:

$$\sum_i x_{i(s)} \cdot d\mu_{i(s)}^* - \sum_i x_{i(s)} \cdot d\mu_i = 0 \quad (6a)$$

where μ_i (J/mol) is the chemical potential of component i in the equilibrium bulk phases and $d\mu_i \equiv \left(\frac{\partial \mu_i}{\partial x_{B(s)}} \right)_{p,T,x_i} \cdot dx_{B(s)}$. As

μ_i depends only on bulk compositions of the equilibrium phases, temperature, and pressure but is obviously independent of the surface composition, the second term of eq 6a is zero. The first term of eq 6a is zero due to eq 2n, and this is how the validity of eq 6a is proven. Now, let us make some rearrangements in eq 6a:

$$\sum_i x_{i(s)} \cdot d(\mu_{i(s)}^* - \mu_i) = 0 \quad (6b)$$

Now, let us recall that according to ref 28, the difference between the reduced surface chemical potential and the bulk chemical potential of any component i equals the partial molar surface excess Gibbs energy of the same component ($\omega_i \cdot \sigma_i$, J/mol) as

$$\mu_{i(s)}^* - \mu_i = \omega_i \cdot \sigma_i \quad (6c)$$

The quantity $\omega_i \cdot \sigma_i$ can be understood as the molar partial surface excess Gibbs energy of component i accompanying its transfer from the bulk of the phase to its surface region (see also eq 2m). Now, let us substitute the right hand side of eq 6c into the parentheses in eq 6b:

$$\sum_i x_{i(s)} \cdot d(\omega_i \cdot \sigma_i) = 0 \quad (6d)$$

Equation 6d is the third surface Gibbs–Duhem equation written for the partial molar surface excess Gibbs energy of component i . For a binary A – B solution, eq 6d simplifies as

$$(1 - x_{B(s)}) \cdot \frac{d(\omega_A \cdot \sigma_A)}{dx_{B(s)}} + x_{B(s)} \cdot \frac{d(\omega_B \cdot \sigma_B)}{dx_{B(s)}} = 0 \quad (6e)$$

When the Butler eq 2u is substituted into eq 6e to replace both σ_A and σ_B by σ , then this modified eq 6e can be simplified by dividing its sides by σ , and then eq 6e is simplified to eq 3c, proven above. This can be considered as another way to prove the validity of eq 6e. Now, let us rearrange eqs 2v and 2w and write the following model equations for $\omega_A \cdot \sigma_A$ and $\omega_B \cdot \sigma_B$:

$$\omega_A \cdot \sigma_A = \omega_A^o \cdot \sigma_A^o + R \cdot T \cdot \ln \frac{1 - x_{B(s)}}{1 - x_B} + L \cdot (k \cdot x_{B(s)}^2 - x_B^2) \quad (6f)$$

$$\omega_B \cdot \sigma_B = \omega_B^o \cdot \sigma_B^o + R \cdot T \cdot \ln \frac{x_{B(s)}}{x_B} + L \cdot [k \cdot (1 - x_{B(s)})^2 - (1 - x_B)^2] \quad (6g)$$

Let us take the derivatives of eqs 6f and 6g by $x_{B(s)}$:

$$\frac{d(\omega_A \cdot \sigma_A)}{dx_{B(s)}} = -\frac{R \cdot T}{1 - x_{B(s)}} + 2 \cdot L \cdot k \cdot x_{B(s)} \quad (6h)$$

$$\frac{d(\omega_B \cdot \sigma_B)}{dx_{B(s)}} = \frac{R \cdot T}{x_{B(s)}} - 2 \cdot L \cdot k \cdot (1 - x_{B(s)}) \quad (6i)$$

Now, let us substitute eqs 6h and 6i into eq 6e:

$$(1 - x_{B(s)}) \cdot \left(-\frac{R \cdot T}{1 - x_{B(s)}} + 2 \cdot L \cdot k \cdot x_{B(s)} \right) + x_{B(s)} \cdot \left(\frac{R \cdot T}{x_{B(s)}} - 2 \cdot L \cdot k \cdot (1 - x_{B(s)}) \right) = 0 \quad (6j)$$

Rearranging eq 6j, the identity $0 = 0$ is obtained, proving that the model eqs 6f and 6g satisfy the third surface Gibbs–Duhem equation, i.e., the Butler model written by eqs 2v and 2w, are reasonable model equations.

3.4. Derivation of the Fourth Surface Gibbs–Duhem Equation. Now let us apply our previous result:²¹

$$d\sigma = \left(\frac{d\sigma}{dx_{i(s)}} \right)_{p,T,x_i} \cdot dx_{i(s)} = 0. \text{ This is because in equilibrium,}$$

nature seeks for minimum Gibbs energy, including minimum surface tension, which is achieved by adjusting the surface composition of the solutions (for more details, see ref 21). Note that the following three claims are valid at the same time for surface equilibrium: (i) the chemical potential of each component should be identical in all bulk phases and along all interfaces (after Gibbs), (ii) the partial interfacial energies of all components should be identical along each interface (after Butler), and (iii) all interfacial energies have their possible minimum values (after ref 21). Now, let us substitute $d\sigma = 0$ into the first surface Gibbs–Duhem eq 2k to obtain the fourth surface Gibbs–Duhem equation:

$$\sum_i x_{i(s)} \cdot d\mu_{i(s)} = 0 \quad (7a)$$

According to Gibbs, the chemical potential of any component i should be identical in equilibrium in all bulk phases and along all interfaces, i.e., one can write

$$\mu_{i(s)} = \mu_i \quad (7b)$$

Substituting eq 7b into eq 7a and applying the model eqs 1m and 1n, the final result $0 = 0$ follows in the same way as shown above, i.e., it is proven that the regular solution model applied to the surface region obeys the fourth surface Gibbs–Duhem equation. The same conclusion follows if the last terms of eqs 1m and 1n are extended to the Redlich–Kister polynomial.^{36–38}

Finally, let us conclude that the Gibbs–Duhem equation can be extended to all four partial molar surface quantities known to us: the reduced surface chemical potential ($\mu_{i(s)}^*$, eq 2n), the partial molar surface area (ω_i , eq 3c), the partial molar excess surface Gibbs energy ($\omega_i \cdot \sigma_i$, eq 6e), and the surface chemical potential ($\mu_{i(s)}$, eq 7a).

4. CONCLUSIONS

In this paper, the Gibbs–Duhem equation is extended to the partial molar surface thermodynamic properties of solutions by making the sum of mole fractions of the components in the surface region of bulk solutions multiplied by different partial molar surface quantities equal to zero if summation is taken by all components. The following four partial molar surface properties were found to obey the surface Gibbs–Duhem equation: (i) the reduced surface chemical potential, (ii) the partial molar surface area, (iii) the partial molar excess surface Gibbs energy, and (iv) the surface chemical potential.

The reduced surface chemical potential is defined as the sum of the surface chemical potential and the partial surface area multiplied by surface tension; its model equation suggested by us recently²⁸ is found to obey the first surface Gibbs–Duhem equation. In this way, this model equation was found to be valid.

However, the model equation suggested by us recently for the partial molar surface area²⁸ is found to contradict the second surface Gibbs–Duhem equation, i.e., it is found wrong. In this paper, new (and simpler) model equations for the partial molar surface areas are found to obey the second surface Gibbs–Duhem equation. These new model equations are expected to improve the practical application of the Butler equations further.

Applying the third surface Gibbs–Duhem equation, the general form of the Butler equation was further confirmed. Finally, applying the fourth surface Gibbs–Duhem equation, it is shown that in equilibrium, nature seeks for minimum surface tension, which is achieved by adjusting the surface composition of solutions.

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Notes

The authors declare no competing financial interest.

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