

## Examination of the Butler Equation for the Surface Tension of Liquid Mixtures

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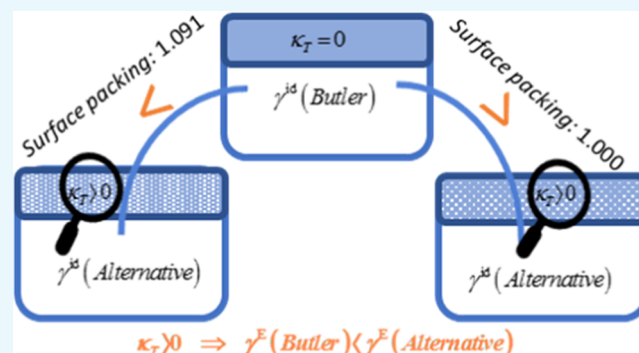


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**ABSTRACT:** The classical Butler equation used to describe surface tension and the surface composition of liquid mixtures is revisited. A straightforward derivation is presented, separating basic chemical thermodynamics and assumptions proper to Butler's model. This model is shown to conceal an approximation not recognized by other researchers. The shortcoming identified consists of not allowing surface standard values to vary with surface tension by virtue of the changing composition. A more rigorous equation is derived and shown to yield the Butler equation in case of incompressible surface phases. It is concluded that the Butler equation slightly overestimates ideal surface tensions. Butler's surface-phase concentrations of the surface-active component are also slightly overestimated in the surface-active component dilute range, being just underestimated at higher concentrations. Despite this, Butler's model stands as a very good standard due to its versatility.



## INTRODUCTION

Predicting the surface tension and the composition of layers overlying liquid mixtures has been the goal of much research over more than a century.<sup>1,2</sup> The renowned Gibbs adsorption isotherm<sup>2–5</sup> (GAI) is a fundamental equilibrium equation that is the foundation stone of this field of inquiry. However, in the case of a binary mixture, GAI only links the surface tension to the relative adsorption, which is the difference between adsorption of one component and that of the other.<sup>5</sup> Among the milestones in this pursuit, the Butler equation<sup>6</sup> published in 1932 is of the foremost influence. Indeed, it was not only the first workable proposal for estimating both the surface composition and surface tension but also the starting point for the advancements due to Hoar and Melford,<sup>7</sup> Sprow and Prausnitz,<sup>8</sup> and Kaptay.<sup>9</sup> This notwithstanding, it has been claimed by Rusanov<sup>10</sup> and by Santos and Reis<sup>11,12</sup> that Butler's model is not so rigorous as generally regarded. Furthermore, it has been emphasized by different authors<sup>3,13</sup> that molecular-thermodynamic models must be validated against the GAI, a condition that Radke<sup>3</sup> suspects that is not met by the Butler equation. Present examination of the Butler equation was prompted by Kaptay's<sup>9</sup> recently improved derivation that removed some, not all, previous reservations to its acceptance. A straightforward derivation of the Butler equation is advanced in terms of formal chemical thermodynamics. Properties of the ideal surface region proposed by Butler are carefully examined since the ideal model for liquid mixtures has proven very useful to describe the essential features of mixtures.<sup>14</sup> It will be shown that indeed Butler's original and subsequently improved

derivations conceal an approximation, namely, that the chosen standard state for describing surface energy changes with varying compositions is not a constant.

Based on a previous thermodynamic development,<sup>11,12</sup> an equation for the surface tension of ideal liquid mixtures is concisely derived. This alternative approach accounts for the variation of standard chemical potentials with changing surface tension from its value for a pure component to its current value at the composition of interest. Remarkably, the alternative equation reduces to the classical Butler equation for incompressible surface phases, as claimed by Rusanov<sup>10</sup> on different grounds. A quantitative evaluation of the effect of this hidden approximation is presented for the molecular mixture, water–ethanol, at 298.15 K and for the metallic liquid alloy, copper–tin, at 1400 K and is shown to be insignificant.

## BUTLER EQUATION

**Formal Thermodynamics Derivation.** Considering a physical planar surface phase<sup>15</sup> of molecular components A and B at fixed temperature  $T$  and pressure  $p$  that is in

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thermodynamic equilibrium with an underlying liquid phase, the differential of the surface-phase Gibbs energy is

$$dG^s = -S^s dT + V^s dp + \gamma dA + \mu_A^s dn_A^s + \mu_B^s dn_B^s \quad (1)$$

where  $G$  stands for Gibbs energy,  $S$  for entropy,  $V$  for volume,  $\gamma$  for surface tension,  $A$  for surface area, and  $\mu_i$  and  $n_i$  for chemical potential and the amount of the substance, respectively, of component  $i = A, B$ . The superscript “s” denoting the surface phase is only attached to properties whose equilibrium values are different in both phases.

It follows from eq 1 that

$$\gamma = (\partial G^s / \partial A)_{T, p, n_A^s, n_B^s} \quad (2)$$

$$\mu_B = (\partial G^s / \partial n_B^s)_{T, p, A, n_A^s} \quad (3)$$

The variation of surface Gibbs energy with the composition at constant  $T$  and  $p$  can be established from eq 3 by applying the rule of partial differentiation to introduce an extra restriction. This gives

$$\left( \frac{\partial G^s}{\partial n_B^s} \right)_{T, p, n_A^s} = \left( \frac{\partial G^s}{\partial n_B^s} \right)_{T, p, A, n_A^s} + \left( \frac{\partial A}{\partial n_B^s} \right)_{T, p, n_A^s} \left( \frac{\partial G^s}{\partial A} \right)_{T, p, n_A^s, n_B^s} \quad (4)$$

It has been shown<sup>2,16–18</sup> that the derivative  $(\partial A / \partial n_B^s)_{T, p, n_A^s}$  is the partial molar surface area of B designed for conditions of constant  $T$  and  $p$ , and denoted<sup>18</sup>  $\overline{A}_B(T, p)$

$$\overline{A}_B(T, p) = \left( \frac{\partial A}{\partial n_B^s} \right)_{T, p, n_A^s} \quad (5)$$

Inserting eqs 2, 3, and 5 into eq 4 leads to

$$\mu_B = \left( \frac{\partial G^s}{\partial n_B^s} \right)_{T, p, n_A^s} - \gamma \overline{A}_B(T, p) \quad (6)$$

Equation 6 is not new, but now it has been concisely derived using classical thermodynamics only. This is an important step because the Butler equation is based on it. Furthermore, it is noted that eq 6 is identical to eq 21e of ref 2, eq 13 of ref 9, and eq 2d of ref 19 although a misprint certainly occurred in the last two equations, where  $A$  appears as an extra constraint in the partial derivative of  $G^s$ . For simplicity, the following shorthand is introduced

$$g_B^s = \left( \frac{\partial G^s}{\partial n_B^s} \right)_{T, p, n_A^s} \quad (7)$$

In the bulk phase,  $\mu_B$  is described by

$$\mu_B = \mu_B^* + RT \ln(f_B x_B) \quad (8)$$

where  $R$  is the gas constant and  $f_B$  is the rational activity coefficient of B at mole fraction  $x_B$ ; an asterisk denotes a pure-component property. Hence, the standard state is the pure liquid B.

The equilibrium condition between the surface and bulk phases requires the uniformity of  $\mu_B$  so that from eqs 6 and 8, and considering eq 7, one obtains

$$g_B^s = \mu_B^* + \gamma \overline{A}_B(T, p) + RT \ln(f_B x_B) \quad (9)$$

Equation 9 is valid over the full composition range. Since  $f_B = 1$  for  $x_B = 1$ , then

$$g_B^{*,s} = \mu_B^* + \gamma_B^* A_B^* \quad (10)$$

By noting that  $g_B = (\partial G / \partial n_B)_{T, p, n_A} = \mu_B$ , it follows from eq 10 that  $g_B^{*,s} \neq g_B^* = \mu_B^*$ .

Subtracting eq 10 from eq 9 yields

$$g_B^s = g_B^{*,s} - \gamma_B^* A_B^* + \gamma \overline{A}_B(T, p) + RT \ln(f_B x_B) \quad (11)$$

$$\gamma = \gamma_B^* \frac{A_B^*}{\overline{A}_B(T, p)} + \frac{g_B^s - g_B^{*,s}}{\overline{A}_B(T, p)} - \frac{RT}{\overline{A}_B(T, p)} \ln(f_B x_B) \quad (12)$$

It is remarked that proceeding from eqs 6 to 12 required only well-established chemical thermodynamics (see eq 8) and the phase-equilibria thermodynamics expressed in eq 9. Hence, eq 12 is a rigorous expression for the dependence of surface tension on the mixture composition at constant  $T$  and  $p$  that does not involve any approximation or extra thermodynamic assumption.

Butler's original contribution was to put forward an equation for the difference  $(g_B^s - g_B^{*,s})$ . Assuming that this difference can be expressed by an equation similar to eq 8, for changes with the composition at fixed  $T$  and  $p$ , Butler<sup>6</sup> proposed the following expression

$$g_B^s = g_B^{0,s} + RT \ln(f_B^s x_B^s) \quad (13)$$

where  $g_B^{0,s}$  is the corresponding standard-state value.

From eqs 6, 7, and 13, one obtains

$$\mu_B = g_B^{0,s} - \gamma \overline{A}_B(T, p) + RT \ln(f_B^s x_B^s) \quad (14)$$

Using the artifact  $g_B^{0,s} = g_B^{*,s} + g_B^{0,s} - g_B^{*,s}$  and recalling eq 10, eq 14 leads to

$$\mu_B = \mu_B^* + g_B^{0,s} - g_B^{*,s} - \gamma \overline{A}_B(T, p) + \gamma_B^* A_B^* + RT \ln(f_B^s x_B^s) \quad (15)$$

Hence, this approach implicitly assumes a surface standard chemical potential,  $\mu_B^{0,s}$ , having the form

$$\mu_B^{0,s} = \mu_B^* + g_B^{0,s} - g_B^{*,s} - \gamma \overline{A}_B(T, p) + \gamma_B^* A_B^* \quad (16)$$

However, Butler considered  $g_B^{0,s}$  to be a constant, independent of the surface-phase composition and thus equal to  $g_B^{*,s}$ . Therefore, from eqs 12 and 13 one obtains the commonly accepted form of the Butler equation

$$\gamma = \gamma_B^* \frac{A_B^*}{\overline{A}_B(T, p)} + \frac{RT}{\overline{A}_B(T, p)} \ln \left( \frac{f_B^s x_B^s}{f_B x_B} \right) \quad (17)$$

In accordance with this treatment, Butler's standard chemical potential,  $\mu_B^{0,s}(\text{Butler})$ , becomes

$$\mu_B^{0,s}(\text{Butler}) = \mu_B^* - \gamma \overline{A}_B(T, p) + \gamma_B^* A_B^* \quad (18)$$

It is interesting to note that Butler's approach still makes some allowance for a change in the value of the surface standard chemical potential with varying surface compositions.

It is emphasized that in the abovementioned derivation of the Butler equation, no assumption was made regarding the

surface-phase thickness, in agreement with the improved derivation of the Butler equation recently achieved by Kaptay<sup>9</sup> without assuming a surface monolayer. This notwithstanding, why some authors<sup>3,10–12</sup> have argued that the Butler equation still contains an approximation? If so, it must be found in a hidden assumption within eq 13. To clarify this matter, the focus is directed to Butler's ideal surface phase.

The ideal model<sup>14</sup> acquires special relevance in surface thermodynamics because experimentally, the surface-region composition is not easily accessible.<sup>20–22</sup> Since for an ideal liquid mixture according to Raoult's law,  $x_B^{(\text{ideal})} = x_B^{(\text{real})}$ , then the corresponding ideal surface phase should be defined so that  $x_B^{s(\text{ideal})} = x_B^{s(\text{real})}$ . These equalities hold for equilibrium attained from the joint conditions  $\mu_B^{(\text{ideal})} = \mu_B^{s(\text{ideal})}$  and  $\mu_B^{(\text{real})} = \mu_B^{s(\text{real})}$ .<sup>23</sup>

According to Butler, the ideal model for the surface region is obtained from eq 13 by setting  $f_B^s = 1$

$$g_B^{\text{id},s} = g_B^{\text{id},0,s} + RT \ln x_B^s \quad (19)$$

and from eq 17

$$\gamma^{\text{id}} = \gamma_B^* \frac{A_B^*}{\bar{A}_B^{\text{id}}(T, p)} + \frac{RT}{\bar{A}_B^{\text{id}}(T, p)} \ln \left( \frac{x_B^s}{x_B^*} \right) \quad (20)$$

To progress, pure molar and ideal partial molar surface areas need to be modeled.<sup>24</sup> Usually, they are calculated from well-known relationships as proportional to some power of the pure molar volume<sup>2,8,9,11,19</sup> or the partial molar volume in the ideal bulk phase.<sup>2,8,9,19</sup> Since the latter does not vary with the composition, then  $\bar{A}_B^{\text{id}}(T, p) = A_B^*$  and eq 20 simplifies to

$$\gamma^{\text{id}} = \gamma_B^* + \frac{RT}{A_B^*} \ln \left( \frac{x_B^s}{x_B^*} \right) \quad (21)$$

Noting that an analogous expression holds for component A

$$\gamma^{\text{id}} = \gamma_A^* + \frac{RT}{A_A^*} \ln \left( \frac{x_A^s}{x_A^*} \right) \quad (22)$$

equating eqs 21 to 22 allows the estimate Butler's surface-phase composition by solving the nonexplicit expression<sup>25,26</sup>

$$\ln \left( \frac{(x_B^s/x_B^*)^{r_{A/B}}}{(1 - x_B^s)/(1 - x_B^*)} \right) = \frac{(\gamma_A^* - \gamma_B^*)A_A^*}{RT} \quad (23)$$

where  $r_{A/B} = A_A^*/A_B^*$ .

Butler's ideal surface tensions are then obtained by inserting these  $x_B^s$  values in eq 21.

Alternatively, solving eq 21 for  $x_B^s$  and eq 22 for  $x_A^s$  and considering that  $x_A^s + x_B^s = 1$ , a nonexplicit equation is obtained for the calculation of  $\gamma^{\text{id}}$ . Using these values in eq 21 gives  $x_B^s$ . In fact, this alternative way is the most frequently employed. However, it is not certain that Butler's ideal surface-phase compositions thus calculated, and which should be used in eq 19, match those of the corresponding real surface phase. In other words, it is legitimate to look for hidden assumptions in the modern derivation of ideal Butler equations leading to eqs 21 and 22. In addition to equating  $\bar{A}_B^{\text{id}}(T, p)$  in eq 20 to  $A_B^*$ , there is no guarantee that the standard value  $g_B^{\text{id},0,s}$  in eq 19 is rigorously composition independent. Indeed, at fixed  $T$  and  $p$ , standard states in the ideal surface phase with composition  $x_B^s$  should be the pure liquid components under the surface tension of the ideal mixture at that composition because, as

demonstrated by Rudisill and LeVan,<sup>13</sup> only these pure-component standard states satisfy the GAI.

Finally, it is noticed that  $G^s$  in eq 1 is defined as the Legendre transform of the surface-phase internal energy,  $U^s$ , with respect to the variables  $T$  and  $p$ ,  $G^s = U^s - TS^s + pV^s$ . Guggenheim<sup>27</sup> made a different choice by introducing the surface-phase transformed Gibbs energy, herein denoted  $G'^s$ , defined as  $G'^s = U^s - TS^s + pV^s - \gamma A = G^s - \gamma A$ . However, it is paradoxical that using the differential of  $G'^s$  does not lead to the useful Butler equation.

**Hidden Approximation.** The suspected variation of  $g_B^{\text{id},0,s}$  with the composition can be estimated using the Taylor formula for a single variable around  $g_B^{*,s}$ , which provides a sound mathematical answer to this question. Its application gives

$$g_B^{\text{id},0,s} = g_B^{*,s} + \sum_{n=1}^{\infty} \frac{(\gamma^{\text{id}} - \gamma_B^*)^n}{n!} \left( \frac{\partial^n g_B^{*,s}}{\partial (\gamma_B^*)^n} \right)_{T,p} \quad (24)$$

Differentiation of eq 10 in order of  $\gamma_B^*$  gives

$$\left( \frac{\partial g_B^{*,s}}{\partial \gamma_B^*} \right)_{T,p} = \left( \frac{\partial \mu_B^*}{\partial \gamma_B^*} \right)_{T,p} + A_B^* + \gamma_B^* \left( \frac{\partial A_B^*}{\partial \gamma_B^*} \right)_{T,p} \quad (25)$$

The Gibbs–Duhem equation for the surface phase of pure liquid B is<sup>27</sup>

$$S^{*,s}dT - V^{*,s}dp + A_B^*d\gamma_B^* + d\mu_B^* = 0 \quad (26)$$

Division by  $d\gamma_B^*$  at fixed  $T$  and  $p$  gives

$$\left( \frac{\partial \mu_B^*}{\partial \gamma_B^*} \right)_{T,p} = -A_B^* \quad (27)$$

Hence, eq 25 simplifies to

$$\left( \frac{\partial g_B^{*,s}}{\partial \gamma_B^*} \right)_{T,p} = \gamma_B^* \left( \frac{\partial A_B^*}{\partial \gamma_B^*} \right)_{T,p} \quad (28)$$

Singling out the first summation term in eq 24 and considering eq 28 leads to

$$g_B^{\text{id},0,s} = g_B^{*,s} + (\gamma^{\text{id}} - \gamma_B^*) \gamma_B^* \left( \frac{\partial A_B^*}{\partial \gamma_B^*} \right)_{T,p} + \sum_{n=2}^{\infty} \frac{(\gamma^{\text{id}} - \gamma_B^*)^n}{n!} \left( \frac{\partial^n g_B^{*,s}}{\partial (\gamma_B^*)^n} \right)_{T,p} \quad (29)$$

By noting that  $(\partial A_B^*/\partial \gamma_B^*)_{T,p} > 0$  is a thermodynamic requirement for a stable surface phase,<sup>28</sup> even disregarding the higher-order terms of Taylor expansion, one concludes that  $g_B^{\text{id},0,s} \neq g_B^{*,s}$  for  $x_B^s < 1$ . In other words, Butler's assumption of constant standard states  $g_i^{0,s}$  while the composition is changed at fixed  $T$  and  $p$  conceals a presumably small approximation.

On the other hand, Butler's approach leading to eq 20 for  $\gamma^{\text{id}}$  does not provide a clue to calculate  $\bar{A}_B^{\text{id}}(T, p)$ , which has been considered constant and equal to  $A_B^*$ . However, using an advanced thermodynamic treatment,<sup>18</sup>  $\bar{A}_B^{\text{id}}(T, p)$  and  $\bar{A}_A^{\text{id}}(T, p)$  have been calculated for the system water (A)–ethanol (B) at 298 K and shown to vary slightly with the composition. Over the full range from pure water to pure

ethanol,  $\overline{A}_A^{\text{id}}(T, p)$  increases 6% and  $\overline{A}_B^{\text{id}}(T, p)$  decreases 2% (see Table S2 of ref 18).

## ■ ALTERNATIVE EQUATION

**Ideal Surface Phase.** According to the Lewis–Randall formulation of chemical thermodynamics, the chemical potential of B in a bulk ideal mixture is

$$\mu_B^{\text{id}} = \mu_B^*(T, p) + RT \ln x_B \quad (30)$$

It is reasonable to base the formulation of surface ideality on the following expression<sup>11–13</sup>

$$\mu_B^{\text{id}} = \mu_B^{\text{id},0,s}(T, p, \gamma^{\text{id}}) + RT \ln x_B^s \quad (31)$$

Then, at equilibrium

$$\mu_B^* - \mu_B^{\text{id},0,s}(T, p, \gamma^{\text{id}}) = RT \ln \left( \frac{x_B^s}{x_B} \right) \quad (32)$$

Turning to the Taylor formula, standard chemical potentials become related as follows

$$\mu_B^{\text{id},0,s}(T, p, \gamma^{\text{id}}) = \mu_B^* + \sum_{n=1}^{\infty} \frac{(\gamma^{\text{id}} - \gamma_B^*)^n}{n!} \left( \frac{\partial^n \mu_B^*}{\partial (\gamma_B^*)^n} \right)_{T,p} \quad (33)$$

Separating the first term and considering eq 27 give

$$\begin{aligned} \mu_B^{\text{id},0,s}(T, p, \gamma^{\text{id}}) &= \mu_B^* - (\gamma^{\text{id}} - \gamma_B^*) A_B^* \\ &\quad - \sum_{n=2}^{\infty} \frac{(\gamma^{\text{id}} - \gamma_B^*)^n}{n!} \left( \frac{\partial^{(n-1)} A_B^*}{\partial (\gamma_B^*)^{(n-1)}} \right)_{T,p} \end{aligned} \quad (34)$$

Assuming constant surface thickness of a pure liquid, it is shown in the Supporting Information that<sup>4,11</sup>

$$\left( \frac{\partial A_B^*}{\partial \gamma_B^*} \right)_{T,p} = - \frac{A_B^*}{V_B^*} \left( \frac{\partial A_B^*}{\partial p} \right)_T \quad (35)$$

and

$$\begin{aligned} \left( \frac{\partial^{(n-1)} A_B^*}{\partial (\gamma_B^*)^{(n-1)}} \right)_{T,p} &= (n-1)! A_B^* \left[ - \frac{1}{V_B^*} \left( \frac{\partial A_B^*}{\partial p} \right)_T \right]^{(n-1)} \\ &= -(n-1)! \frac{V_B^* A_B^*}{(\partial A_B^* / \partial p)_T} \left[ - \frac{1}{V_B^*} \left( \frac{\partial A_B^*}{\partial p} \right)_T \right]^{(n-1)} \end{aligned} \quad (36)$$

Inserting the latter result into eq 34 leads to

$$\begin{aligned} \mu_B^{\text{id},0,s}(T, p, \gamma^{\text{id}}) &= \mu_B^* - (\gamma^{\text{id}} - \gamma_B^*) A_B^* + \frac{V_B^* A_B^*}{(\partial A_B^* / \partial p)_T} \\ &\quad \sum_{n=2}^{\infty} \frac{(\gamma^{\text{id}} - \gamma_B^*)^n}{n} \left[ - \frac{1}{V_B^*} \left( \frac{\partial A_B^*}{\partial p} \right)_T \right]^{(n-1)} \end{aligned} \quad (37)$$

Recalling the series expansion

$$\sum_{n=2}^{\infty} \frac{x^n}{n} = -\ln(1-x) - x, \quad |x| < 1 \quad (38)$$

and setting the variable  $x$  as

$$x = - \frac{(\gamma^{\text{id}} - \gamma_B^*)}{V_B^*} \left( \frac{\partial A_B^*}{\partial p} \right)_T \quad (39)$$

one finds that

$$\begin{aligned} \mu_B^{\text{id},0,s}(T, p, \gamma^{\text{id}}) &= \mu_B^* - \frac{V_B^* A_B^*}{(\partial A_B^* / \partial p)_T} \\ &\quad \ln \left[ 1 + \frac{(\gamma^{\text{id}} - \gamma_B^*)}{V_B^*} \left( \frac{\partial A_B^*}{\partial p} \right)_T \right] \end{aligned} \quad (40)$$

Finally, combining eqs 32 and 40 gives

$$\frac{V_B^*}{(\partial A_B^* / \partial p)_T} \ln \left[ 1 + \frac{(\gamma^{\text{id}} - \gamma_B^*)}{V_B^*} \left( \frac{\partial A_B^*}{\partial p} \right)_T \right] = \frac{RT}{A_B^*} \ln \left( \frac{x_B^s}{x_B} \right) \quad (41)$$

Bearing in mind that  $e^{(c \ln z)} = z^c$ , eq 41 is transformed into

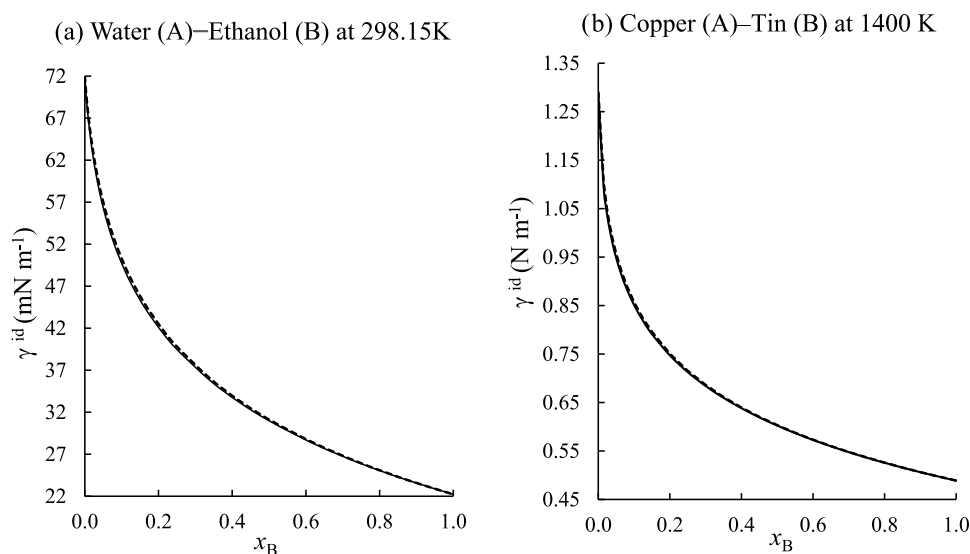
$$x_B^s = x_B \left[ 1 + \frac{(\gamma^{\text{id}} - \gamma_B^*)}{V_B^*} \left( \frac{\partial A_B^*}{\partial p} \right)_T \right]^{(V_B^* A_B^* / RT (\partial A_B^* / \partial p)_T)} \quad (42)$$

where  $(\partial A_B^* / \partial p)$  can be estimated using the model-based eq S7.

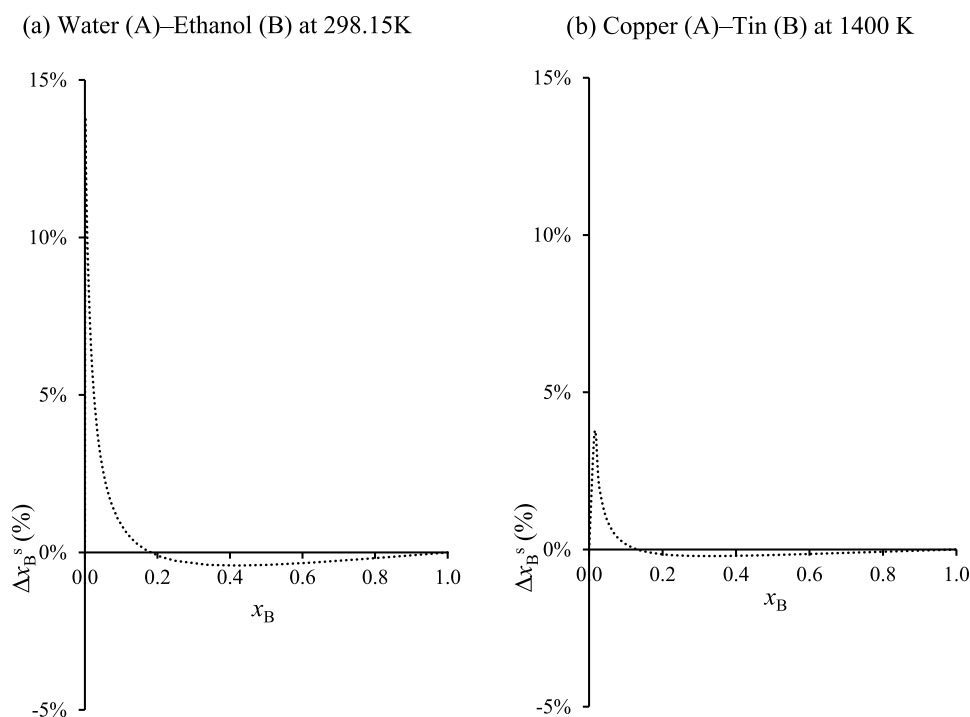
Since an analogous equation holds for  $x_A^s$  and recalling  $x_A^s + x_B^s = 1$ ,  $\gamma^{\text{id}}$  can be computed from the resulting nonexplicit expression and thereby the surface-phase composition calculated. Although eqs 40 and 42 are not new,<sup>11</sup> the foregoing proof is shorter. Note that this alternative approach is not amenable to yield an explicit equation for  $\gamma^{\text{id}}$  as eq 21 nor an equation for  $x_B^s$  similar to eq 23, which are both proper to Butler's approach.

## ■ RESULTS AND DISCUSSION

Considering a given binary system at fixed  $T$ ,  $p$ , and  $x_B$ , it is clear that calculated values for  $x_B^s$  and  $\gamma^{\text{id}}$  depend on the chosen model, the Butler equation, or the alternative equation. However, these models are not too dissimilar. Indeed, inasmuch as  $\ln(1-x) \approx -x$  for  $|x| < 1$ ,  $x$  being given by eq 39, eq 41 reduces to eq 21, a fact appreciated by other authors,<sup>29,30</sup> and consequently  $x_B^s$  (Butler's approach)  $\approx x_B^s$  (alternative approach). Considering eqs 39, S9, and S10, this equivalence is best for binary systems of components with not significantly different surface tensions, large molar volumes, and low isothermal compressibilities. This same outcome arises from retaining only the first term of Taylor expansion in eq 33, which amounts to considering  $(\partial A_B^* / \partial p)_T$  null (see eq 36). Equivalently, in view of eqs 28 and 35,  $(\partial g_B^{*,s} / \gamma_B^*)_{T,p} = 0$  for an incompressible surface phase so that from eq 29,  $g_B^{\text{id},0,s} = g_B^{*,s}$ , which is Butler's nonstated assumption. This is an important result on the account of Rusanov's harsh criticism of Butler's model "because it involves compressible bulk phases and incompressible monolayer".<sup>10</sup> It is underlined that the alternative model makes provision for compressible surface phases. Present arguments have been based on ideal surface properties that provide reference values for estimating excess quantities. Excess surface tensions  $\gamma^E = \gamma - \gamma^{\text{id}}$  are linked to surface-phase activity coefficients.<sup>31</sup> Hence, any approximation made while computing Butler's ideal surface tension values will



**Figure 1.** Ideal surface tension,  $\gamma^{\text{id}}$ , versus the bulk mole fraction of component B,  $x_B$ . Solid lines for the alternative model and broken lines for Butler's model. Surface packing factor  $f_i(\text{hcp}) = 1.091$ .

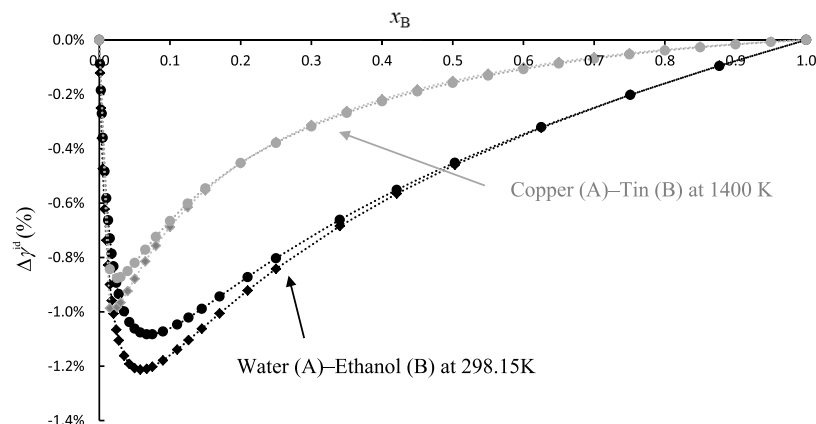


**Figure 2.** Difference between estimated surface mole fractions by the alternative and Butler's equation expressed as % deviation from the alternative model. Surface packing factor  $f_i(\text{hcp}) = 1.091$ .

be included in Butler's activity coefficients to describe real surfaces.

**Comparison of Models.** Two binary systems were used to compare ideal surface tension and the surface composition predicted by Butler's and alternative equations. Labeling B as a surface-active constituent, the examined systems are water (A)–ethanol (B) at 298.15 K, which is a mixture of molecular liquids, and the liquid alloy copper (A)–tin (B) at 1400 K. Molar surface areas of the pure components were estimated on the basis of hexagonally close-packed disks in a monolayer of close-packed equal spheres (packing factor  $f_i(\text{hcp}) = 1.091$ );<sup>7,32</sup> additional calculations were made using the packing factor for cubic cells  $f_i(\text{cc}) = 1.000$ , as recommended by

Kaptay<sup>19,33</sup> for simple liquid metals, and which is also employed for molecular liquids.<sup>8</sup> The required physical data for water and ethanol (refs 34–36) and for copper and tin (refs 37–39) are presented in Table S1. For Butler's model values,  $x_B^s$  was calculated using eq 23, and then eq 21 was employed to obtain  $\gamma^{\text{id}}$ . For the alternative model values, an equivalent procedure was used, namely, resorting to eq 42 and its analogue for  $x_A^s$  and solving  $x_A^s + x_B^s = 1$  for  $\gamma^{\text{id}}$ . Plots of ideal surface tension ( $f_i(\text{hcp}) = 1.091$ ) and the difference between surface compositions, expressed as % deviation, calculated by both models against the bulk concentration are shown in Figures 1 and 2, respectively, for both binary systems.



**Figure 3.** Effect of the packing factor  $f_i$ -value on the difference between calculated ideal surface tensions by the alternative and Butler's models, expressed as % deviation from the alternative model for (♦),  $f_i(\text{hcp}) = 1.091$  and (●),  $f_i(\text{cc}) = 1.000$ .

Figure 1 shows that Butler's ideal surface tensions are marginally larger than those calculated with the alternative equation. Consequently, the corresponding excess surface tensions are slightly different.

The unexpected behavior observed in Figure 2 deserves some clarification. Indeed, solving eq 21 for Butler's  $x_B^s$  values, dividing by eq 42 for the alternative  $x_B^s$  values, and taking logarithms and resorting to the series expansion  $\ln(1 - x) = -\sum_{n=1}^{\infty} \frac{x^n}{n}$  ( $|x| \leq 1$  and  $x$  given by eq 39), yield

$$\ln\left(\frac{x_B^s(\text{Butler})}{x_B^s(\text{alternative})}\right) = \frac{(\gamma^{\text{id}}(\text{Butler}) - \gamma^{\text{id}}(\text{alternative}))A_B^*}{RT} + \text{remainder} \quad (43)$$

Analysis of eq 43 shows that the first term on the r.h.s. is positive and the remainder negative; the magnitude of the remainder decreases with increasing  $x_B$  since  $(\gamma^{\text{id}} - \gamma_B^*)$  varies between  $(\gamma_A^* - \gamma_B^*)$  and zero. Therefore,  $x_B^s(\text{Butler}) < x_B^s(\text{alternative})$  for low  $x_B$  values and opposite for large  $x_B$  values. Moreover, since these differences are negligible, particularly for  $x_B \geq 0.2$ , one may conclude that Butler's model introduces unimportant errors in the calculated surface-phase compositions.

The impact of the adopted packing factor on theoretical calculations of ideal surface tensions was evaluated for both representative binary systems. The outcome of this analysis is condensed in Figure 3, which shows that a smaller  $f_i$  entails smaller  $\gamma^{\text{id}}$  values as well as smaller differences between alternative and Butler's models. The generally small differences depend on the composition, being imperceptible at high concentrations of the surface-active component. The chemical nature of the mixture components having a noteworthy effect on  $\gamma^{\text{id}}$  estimates which depend on the computed molar surface areas, that are calculated using  $f_i$  values. In sum, for both binary systems,  $\gamma^{\text{id}}(\text{Butler}, f_i = 1) > \gamma^{\text{id}}(\text{alternative}, f_i = 1) > \gamma^{\text{id}}(\text{Butler}, f_i = 1.091) > \gamma^{\text{id}}(\text{alternative}, f_i = 1.091)$ , despite an overall modest impact of the packing factor value on the reliability of Butler's model.

Finally, one may speculate about the major factor contributing to the deviation of Butler's model from the alternative approach herein presented. Clearly, it is the isothermal compressibility of the pure compounds, which is

of the order of 1 GPa<sup>−1</sup> for molecular liquids,<sup>40</sup> while not amounting to more than a few 0.01 GPa<sup>−1</sup> for liquid metals.<sup>41</sup> The magnitude difference between isothermal compressibilities offsets the pure-component surface tension differences  $\gamma_{\text{H}_2\text{O}}^* - \gamma_{\text{EtOH}}^* = 49.72 \text{ mN m}^{-1}$  and  $\gamma_{\text{Cu}}^* - \gamma_{\text{Sn}}^* = 801 \text{ mN m}^{-1}$ , resulting in minor deviations of  $\gamma^{\text{id}}$  and  $x_B^s$  for both systems.

## CONCLUSIONS

The Butler equation merits a good score in this examination. As widely acknowledged, it has provided a good basis to estimate the surface tension and the surface-phase composition of planar liquid mixtures. The Butler equation is, herein, deduced using formal thermodynamics allowing the disclosure of an underlying hidden approximation. This consists of implicitly assuming that in the thermodynamic description of surface phases at fixed  $T$  and  $p$ , the standard-state values of mixture constituents are not affected by the surface tension variation that accompanies composition changes. An alternative equation allowing for the effect of surface tension on surface standard chemical potentials is worked out. It is shown that it reduces to the conventional Butler equation when molar surface areas of the pure components are not affected by surface tension or pressure variations. Interestingly, this conclusion corroborates Rusanov's<sup>10</sup> inference that the Butler equation is only exact for incompressible surface phases.

Summing up, even though imperfect, the Butler equation has the advantage of providing an explicit and mathematically simple expression for the surface tension of liquid mixtures. This feature has allowed various surface phenomena to be successfully modeled<sup>2,19,26,42–46</sup> while employing the Butler equation. It has been, herein, demonstrated that it can continue to be confidently applied because of the small, largely inconsequential numerical errors involved.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c02606>.

Derivation of eqs 35 and 36 and physical properties of water and ethanol at 298.15 K and of liquid metal copper and tin at 1400 K (Table S1) (PDF)

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## Notes

The authors declare no competing financial interest.

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