

# Comment on “Surface thermodynamics reconsidered. Derivation of the Gokhshtein relations from the Gibbs potential; and a new approach to surface stress” by Stephen Fletcher

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**Abstract** The present article comments on the article of Stephen Fletcher (Journal of Solid State Electrochemistry Volume 18, Issue 5, pp 1231–1238). The analysis deals with the validity of equation (31 or 40) of the latter for an ideally polarisable interface.

Stephen Fletcher presents [1] a theoretical work concerning surface thermodynamics. The article deals with a subject that has generated vivid discussions in the literature, concerning the validity of Gokhshtein relations and their derivation. In the present approach, the author proposes a derivation from the Gibbs potential, in the special case where the electrode/solution interface is ideally polarizable. Leaving aside the problem of stress, which is out of our expertise field, the present comment is related to equation<sup>1</sup> (F31)–(F40) in this article that reads:

$$\partial \bar{\mu}_i = z_i e_0 \partial E \quad (1)$$

where  $\bar{\mu}_i$  is the electrochemical potential of the  $i$ -specie,  $z_i$  and  $e_0$  are the charge number (dimensionless) of  $i$ -specie and the elementary charge, respectively, and  $E$  is the electrode potential. Equations (F31)–(F40) is applied to an ideally polarizable electrode/solution interface model.

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Our main concern is that Eq. (1) is not generally valid for an ideally polarisable interface, as shown below. With this purpose, we start from equation (4.3.5) of Trasatti and Parsons<sup>2</sup> that states:

$$e_0 \varepsilon = (\bar{\mu}_B^\alpha / z_B) - (\bar{\mu}_C^\beta / z_C) \quad (2)$$

where  $\varepsilon$  is the generalized potential,  $\bar{\mu}_j^i$  is the electrochemical potential of the  $j$ -specie in the  $i$ -phase, and  $z_j$  is the charge of the  $j$ -specie.  $\varepsilon$  is related to the measurable potential difference via an additive constant, which depends on the nature of the reference electrode chosen. Note that we have defined the electrochemical potential in terms of the free energy per particle and not per mole of particles, so that the elementary charge  $e_0$  is used on the *lhs* of Eq. (2) instead of Faraday constant.  $B$  and  $C$  correspond to charged species located in phases  $\alpha$  and  $\beta$ , respectively. If  $\alpha$  and  $\beta$  are chosen to be the solution ( $S$ ) and the metal ( $M$ ) phases, respectively, then  $C$  and  $B$  may be chosen to be the electrons and some ionic species of interest, respectively, that we denote with the subindices  $e$  and  $i_e$  respectively.

Thus, Eq. (2) may be rewritten by:

$$e_0 \varepsilon = [(\mu_{i_e}^S / z_i) + \mu_e^M] + [e_0 (\varphi^S - \varphi^M)] \quad (3)$$

where  $\varphi^M$  and  $\varphi^S$  are the Galvani potentials in the bulk metal and solution phases, respectively. If we consider an increment in Eq. (3), assuming that the activities in the bulk phases remain constant, we get:

$$\partial \varepsilon = \partial (\varphi^S - \varphi^M) \quad (4)$$

That reminds us the well-known fact that changes in the inner potential difference at the metal/solution interface can be measured.

On the other hand, from the definition of the electrochemical potential of species,  $\bar{\mu}_i$ :

$$\bar{\mu}_i = \mu + z_i e_0 \varphi \tag{5}$$

we get:

$$\partial \bar{\mu}_i^S = z_i e_0 \partial \varphi^S \tag{6}$$

That is the change of the electrochemical potential of the  $i$ -species will be given by the change of the inner potential of the solution. There is in principle no straightforward argument justifying that the condition of Eq. (4) does necessarily involve Eq. (6).

We now concentrate to analyze the change of  $\varphi^S$  for two different conditions of the metal/solution interphases. In order to change the potential difference ( $\varphi^S - \varphi^M$ ) in the amount  $\partial \varepsilon$ , some charge  $\partial Q$  must be added to the metal. Since the metal/solution interphase is assumed to be ideally polarizable, neither electronic nor ionic charge will flow across it. To screen the field generated by the metal in the solution, a net ionic charge  $-\partial Q'$  will flow to the neighborhood of the metal surface, involving anion (cation) accumulation (depletion) on the solution side of the interface, so as to get a zero field inside the solution phase. Let us introduce the first modeling for the solution. We will assume that the solution is connected to an infinite reservoir of anions/cations with constant electrochemical potential (Grand Canonical conditions). Under these conditions, anions (cations) will flow to (from) the reservoir to the interphase, keeping the rest of the solution neutral. Under these conditions, and if we assume as zero for the electrostatic potential a point located far from the electrochemical cell, the change  $\varphi^S$  will be zero, and  $\partial \bar{\mu}_i^S = 0$ . In other words, if we can

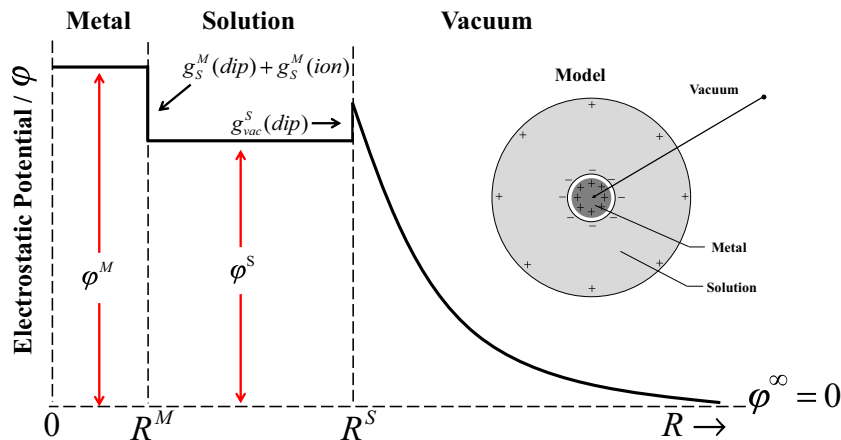
put/take away ions from an infinite reservoir, nothing will change in the solution far away from the electrode surface, and the electrostatic work to bring a charge inside it will remain unchanged with respect to the point previous to the addition of the charge  $\partial Q$ . Thus, under Grand Canonical conditions, we conclude that  $\partial \bar{\mu}_i^S = 0$  for a finite  $\partial \varepsilon$ , something that it is in contradiction with Eq. (1).

We turn now to analyze the Canonical condition for the electrolyte solution. Here, if an electrolyte charge  $-\partial Q'$  flows to the metal/solution interphase, an equivalent charge  $\partial Q'$  must appear somewhere else on the surface of the solution phase, because the ionic charges are mobile in the solution. Since the charge distribution will certainly depend on the geometry of the system, we have adopted the model shown in Fig. 1. We have taken an spherical metal electrode of radius  $R_M$ , surrounded by an also spherical solution phase of radius  $R_S$ . Here, the charge on the metal is  $Q$ . This generates a charge  $-Q$  on the solution side close to the metal and a charge  $Q$  at the metal/vacuum interphase. The potential difference between a point at infinity and a point inside the metal can be written as:

$$\varphi^M - \varphi^\infty = \varphi^M = \frac{Q}{R_S} + g_{vac}^S(dip) + g_S^M(dip) + g_S^M(ion) \tag{7}$$

where  $g_\alpha^\beta(dip)$  denote dipole potentials arising due to the contact between phases  $\alpha$  and  $\beta$ , and  $g_\alpha^\beta(ion)$  is the corresponding potential drop associated with free charges on the phases when the solvent molecules in the interphase are regarded as non-polarizable particles. We will assume that the latter is given by that arising due to a compact ionic double layer. Thus,  $g_S^M(ion) \approx -\frac{Q}{R_S^2} \Delta x$ , where  $\Delta x$  is the thickness of the compact double layer, which is of the order of the diameter of a solvent molecule. In principle,  $g_\alpha^\beta(dip)$  depends on  $Q$ , but we will neglect below this dependence to make an estimation of the relationship between  $\partial(\varphi^S - \varphi^M)$  and  $\partial \varphi^S$ , the quantities involved above in Eqs. (4) and (6). Within the present model,

**Fig. 1** Schematic representation of a metal electrode immersed in an electrolytic solution and the different potentials defined in the text



$\varphi^S$  is given by:

$$\varphi^S = \frac{Q}{R_S} + g_{vac}^S(dip) \tag{8}$$

So  $\varphi^S - \varphi^M$  will be:

$$\varphi^S - \varphi^M = \frac{Q}{R_M^2} \Delta x - g_S^M(dip) \tag{9}$$

Taking increments in Eqs. (8) and (9), we can get  $\partial\varphi^S$  as a function of  $\partial(\varphi^S - \varphi^M)$  according to:

$$\partial\varphi^S = \frac{R_M^2}{R_S \Delta x} \partial(\varphi^S - \varphi^M) \tag{10}$$

which shows that in general  $\partial\varphi^S \neq \partial(\varphi^S - \varphi^M)$ . If  $R_S \rightarrow \infty$ , then  $\partial\varphi^S$  will drop to zero, as discussed above under Grand Canonical conditions, that is the infinitely large solution phase will be able to deal with any finite changes in the charge of the system without altering the Galvani potential inside it. Thus, Eq. (1) remains unjustified.

### Saving the derivation of Gokhshteins equation following Fletcher’s proposal

As we have seen above, Eq. (1) cannot shown to be valid, so it appears that Eq. (FM1) cannot be demonstrated from Eq. (F38). However, we will see that this is possible with a slight modification to it. With this purpose, we will rewrite Eq. (F32) as:

$$dU = TdS - PdV + \gamma dA + \bar{\mu}_i dN_i + \bar{\mu}_e dN_e \tag{11}$$

where besides the ions of  $i$ -type, we have also considered the electrons of the metal as a component of the system.

Using now the definition of Gibbs free energy,  $G = U - TS + PV$  and Eq. (11), we arrive at:

$$dG = -SdT + VdP + \gamma dA + \bar{\mu}_i dN_i + \bar{\mu}_e dN_e \tag{12}$$

If we now assume that the only charged species participating are electrons and  $i$  type species ( $dN_e = z_i dN_i$ ), and constant temperature and pressure conditions we arrive at:

$$dG = \gamma dA + \left( \frac{\bar{\mu}_i}{z_i} + \bar{\mu}_e \right) z_i dN_i = \gamma dA + \left( \frac{\bar{\mu}_i}{z_i} + \bar{\mu}_e \right) dQ \tag{13}$$

Note that this equation is very similar to Eq. (F39), but instead of the electrochemical potential of the species  $i$ , we have a parenthesis which is identical with the *rhs* of Eq. (2), that is a quantity that is directly related to the measurable potential difference. From Eq. (13), which has been proposed by Valicius in reference [2], Eq. (FM1) follows directly using Maxwell relations.

However, the previous derivation remains arbitrarily restricted to a fixed number of charged species (2) and makes no explicit mention of other charged species.

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