

Comment on “Historical development of theories of the electrochemical double layer” by B. B. Damaskin and O. A. Petrii

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It is shown that the *first* and *second* Gokhshtein equations (GEs) were originally derived violating criteria for applications of Maxwell relations and Legendre transformations. Another approach to the derivation of the *second* GE was proposed by Frumkin, but being criticized recently, it also is erroneous. Thus, these equations cannot be accepted in the thermodynamic theory of electrocapillarity. As is said in the comprehensive review [1] “Attention is drawn to several unsolved problems crucial for the future development of electrochemical surface science.”

However, despite significant place taken in [1] by the analysis of the history and the current state of electrocapillarity, the authors [1] do not address a critical and unresolved issue as the applicability of the electrocapillary theory to solid electrodes. Moreover, underlining “the fact that recent discussions...actually considered the problem of a relationship between the surface tension and the reversible surface work for the solid electrode/solution interfaces,” the authors [1] endorsed the concept of Gokhshtein [2, 3] (in [1] in refs. 56, 57) whose method is based on equations called in the literature as the *first* and *second* GEs.

As the authors [1] consider, this method gives “a comparison of the surface tension and the reversible work of surface formation on the level of their derivatives based on the concept of total charge of a perfectly polarizable electrode was carried out by Gokhshtein [56] (here [2]) by the ‘estance method’ which he developed (estance is the derivative of the surface tension of a conducting solid with respect to an electrical variable).” However, a simple check of the original source [2] shows that Gokhshtein has come to erroneous equations as shown below.

To obtain the *first* and *second* GEs, the author [2] introduced the “thermodynamic potentials” as Eq. 4.4.20 in [2]

$$\Psi = F + PV - \sum_k \mu_k n_k \quad (1)$$

for the derivation of the first GE, and Eq. (4.3.1) in [2]

$$\Phi = F + PV - \varphi Q - \sum_k \mu_k n_k \quad (2)$$

for the derivation of the second GE, where Q is the surface charge, φ is the potential difference between the working and reference electrodes, n_k and μ_k are the mole number and chemical potential of independent components, respectively; U , P , and V are the internal energy, pressure, and volume of the system, respectively; the free energy, by definition, is $F = U - TS$.

Using the differential of the free energy (Eq. 4.3.13) [2]

$$dF = -SdT - PdV + \gamma dA + \varphi dQ + \sum_k \mu_k dn_k \quad (3)$$

where γ is called the “surface tension” [2] and A is the surface area, one obtains the differential for (1), as Eq. 4.4.21 [2]

$$d\Psi = -SdT + VdP + Kdl + \varphi dQ - \sum_k n_k d\mu_k \quad (4)$$

where K is the tensile force and l is the length of the electrode in the direction of the force. Accordingly to Eqs. 4.3.7 and 4.3.11 in [2], there exists a relation $Kdl = \gamma dA$, and then Eq. 4 can be rewritten as

$$d\Psi = -SdT + VdP + \gamma dA + \varphi dQ - \sum_k n_k d\mu_k \quad (5)$$

The differential of Eq. 2 is given by Eq. 4.3.14 or 4.3.3 [2],

$$d\Phi = -SdT + VdP + \gamma dA - Qd\varphi - \sum_k n_k d\mu_k \quad (6)$$

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and subsequent concepts [2] are based on manipulations with partial derivatives of these equations.

From Eq. 1 Gokhshtein obtained the *first* GE (Eq. 4.4.22 in [2] incorporated into Eqs. 2–15 [4])

$$(\partial\gamma/\partial Q)_{A,\mu_k,P,T} = (\partial\varphi/\partial A)_{Q,\mu_k,P,T} \quad (7)$$

From Eq. 2, Gokhshtein derived his Eq. 4.3.16 [2] (Eq. 2–13 in [4])

$$(\partial\gamma/\partial\varphi)_{A,\mu_k,P,T} = -(\partial Q/\partial A)_{\varphi,\mu_k,P,T} \quad (8)$$

and from this equation, he derived the *second* GE with $Q=qA$ and $de=dA/A$

$$(\partial\gamma/\partial\varphi)_{A,\mu_k} = -q - (\partial q/\partial e)_{\varphi,\mu_k} \quad (9)$$

where q is the surface charge density. This equation is denoted (4.4.12) in [2] and (2–12) in [4]. All derivations are made as formal Maxwell relations using the basic Eqs. 4 and 6. However, these procedures are not correct.

Actually, as known [5], before constructing Maxwell relations, it is necessary to know what independent variables are implied (to identify a pair of *independent* natural variables) and to establish the thermodynamic potential from which the Maxwell relation is derived. This thermodynamic potential should be a state function called the “characteristic function” in the sense that all thermodynamic properties of homogeneous system can be expressed directly through it and its partial derivatives on appropriating variables. It is important to be sure that natural variables are *independent*. Characteristic functions, by definition, contain all the thermodynamic “information” concerning a given system. Therefore, if the problem of transition from one variable to another arises, such transition may be carried out by means of Legendre transformations but under the condition of conservation of such property of the function as being a characteristic function. Therefore, not every possible formal Legendre transformations can be used to obtain correct Maxwell relations [6]. Now we estimate the conformity of the introduced [2] “thermodynamic potentials” (1) and (2) to the mentioned criteria.

It is easy to see that Eq. 1 is, generally speaking, the *complete* Legendre transform of the free energy $F(T, V, n_k)$ and it is identically zero $\Psi \equiv 0$ [5]. But if the surface tension work γdA and the electrical charging work φdQ are involved in dF [2], the differential (5) and the function Ψ could be quite omitted because in order to construct Maxwell relations for GEs it is enough [5] to use the differential of the free energy (Eqs. 2–14 in [4] or Eq. 4.21 in [2])

$$dF = \gamma dA + \varphi dQ \quad (10)$$

This leads to the first GE (7) that is erroneous because it presents not correct Maxwell relation due to the interdependence between variables A and Q : $Q=qA$ (for details, see [7]). Thus, it is strange that the author introduced Eq. 1, the more so that Eq. 10 was also used in other section of the same book ([2] Eq. 4.21) to derive GEs.

Equation 2 is a formal partial Legendre transform of the function $F(T, V, n_k, Q, A)$ which, however, is not “characteristic function” because the variables Q and A are interdependent: $Q=qA$. Thus, the important criteria given above for correct Legendre transformations are violated and the second GE (9) derived from (2) by constructing formal Maxwell relations is erroneous similarly to that obtained by Frumkin [6] from Eq. 10 (for details, see [7]).

On the contrary, the correct Legendre transform could be constructed using the Gibbs fundamental equation for the internal energy (of course, if the variables A and Q would be independent)

$$dU = TdS - PdV + \gamma dA + \varphi dQ + \sum_k \mu_k dn_k \quad (11)$$

Then the Legendre transform written in systematic notations [5] $G \equiv U [T, P, \gamma, \varphi]$ is the “characteristic function” usually named the Gibbs free energy and the total differential in a surface phase is

$$dG^s = -S^s dT + V^s dP - Ad\gamma - Q^s d\varphi + \sum_k \mu_k^s dn_k^s \quad (12)$$

where the superscript s denotes surface excesses of the respective quantities. However, the actual interdependence of the variables A and Q do not permit to realize this approach. Note, this equation coincides with well known Eq. 1.56.5 in [8] if to remove the electrical work term φdQ . Another approach to the derivation of the *second* GE was proposed by Frumkin [6, pp. 40–48] that also is erroneous and leads to erroneous GEs [7].

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