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ORIGINAL PAPER

Reply to: "Comment by Emmanuel M. Gutman on: Historical development of theories of the electrochemical double layer" [Damaskin BB, Petrii OA (2011) *J Solid State Electrochem*. 15:1317]

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Abstract This publication is a reply to the comment of Professor E.M. Gutman on paper "Historical development of theories of the electrochemical double layer" (J Solid State Electrochem 15:1317, 2011).

In our review [1], an attempt was undertaken to make a historical survey of certain important problems of electrochemical surface science. One of discussed problems concerned the thermodynamic treatment of surface phenomena on solid electrodes and, particularly, the analysis of the relationship between the interface tension and the reversible work of surface formation for the solid electrode/solution interface.

The scopes of that review did not allow us to cover the mentioned field sufficiently broadly and cite all relevant publications. We merely outlined [1] the contribution made by A.Ya. Gokhshtein who had developed an original method for studying the solid electrode/solution boundary in the 1960s–1970s, at the Institute of Electrochemistry in Moscow [2, 3]. He named it the estance method. This method makes it possible to find the dependence of the interface tension on the potential for a solid electrode under elastic strain. Gokhshtein put forward an interpretation of the results obtained by the estance method, which was based on the concept of the difference between the interface tension and the reversible work of surface formation for an isotropic solid. The analysis of equations he derived was beyond the scopes of our review [1].

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In his monograph [4] (pp. 40–43), A.N. Frumkin noted the considerable progress in finding the dependence of the interface tension of a solid electrode on the potential, which was achieved due to the use of the estance method. He mentioned Gokhshtein's data mainly as regards the determination of zero charge potentials (PZC) of solid electrodes by this method; the quantitative relationships were given with the reference to Gokhshtein. It was mentioned that the estance measurements with ac current of different frequencies provide the information on surface properties, which cannot be acquired by other ways; "…however, for the same reason, these measurements cannot be considered as an independent method of PZC determination". According to Frumkin, of fundamental importance is the difference observed between the estance zero and the PZC, which points to the PZC shift at the elastic strain of the solid electrode. For certain systems, e.g., Pb, Bi, Tl, and Cd, this shift is small (not higher than ~0.03 V). However, for elastically strained platinum, the shift of the zero total charge potential reaches a very high value, which requires additional studies. This result together with the anomalously high slope of the estance vs. potential curve at zero estance, which was observed for Cd, failed to attract due attention so far. We believe that it is these observations that are the most interesting and important for both experimental investigations and the theoretical analysis. Frumkin [4] (pp. 43–48) also surveyed critically the numerous known by then attempts to transfer the electrocapillary methods to solid electrodes.

Nowadays, the growing interest in physics and chemistry of surfaces is associated with the appearance of new objects of nanoscience and nanotechnology (nanoparticles, nanotubes, nanowires, thin films, graphene, oxide interfaces, interfaces in biological systems, etc.). As the result, debates were resumed about the Shuttleworth equation [5–18], the latter, according to [5], being "arguably the second most

important equation in surface physics". These debates were directly related to the problem mentioned in [1]. Professor E.M. Gutman took active part in this discussion. It should be mentioned that different opinions were voiced and no consensus was reached so far. Our ideas about certain arguments used in [5–18] will soon appear as a separate publication.

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