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Short communication

REPLY TO "REMARK ON THE PAPER OF S. TRASATTI: THE CONCEPT OF ABSOLUTE ELECTRODE POTENTIAL. AN ATTEMPT AT A CALCULATION", BY A. FRUMKIN AND B. DAMASKIN

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Frumkin and Damaskin's (FD) objections [1] essentially concern the applicability of the term 'absolute electrode potential'. According to their comments, the breaking up of the cell potential E into two electrode potentials is arbitrary and cannot be carried out unambiguously. For this reason, the absolute thermodynamic electrode potential* as defined in the paper under discussion [2]:

$$\epsilon_T(M^+/M) = (\Delta_S^M\phi - \mu_e^M/e) \tag{1}$$

is in fact conditional and not absolute. As a consequence, the work defined by eqn. (1) cannot have a straightforward physical meaning [2]. FD argue that if an arbitrary constant is added to eqn. (1), another electrode potential is obtained:

$$\epsilon_k(M^+/M) = (\Delta_S^M\phi - \mu_e^M/e + k) \tag{2}$$

which, compared to the potential of a reference electrode, still gives the same cell potential E:

$$E = \epsilon_k(M^+/M) - \epsilon_k^0(H^+/H_2) = \epsilon_T(M^+/M) - \epsilon_T^0(H^+/H_2) \tag{3}$$

The conditionality is due to the fact that k in eqn. (2) may take any value.

In the present author's opinion, FD's remarks are only partly founded. They are certainly right as they state that ϵ_T is not an absolute potential. This comes out clearly from the analysis of the relation of eqn. (1) to a real physical work (footnote on p. 319 in ref. 2) although it is agreed that the difference between ϵ_T and ϵ_k is not clearly recognized in the paper under discussion. However, the choice of constant k in eqn. (2) is not arbitrary. This can be proved as follows.

* In ref. 2 the symbol ϵ_{abs} was used for the quantity defined by eqn. (1). Here ϵ_T as used by FD is preferred for the reasons given later.

Let us consider the usual experimental set-up for electrode potential measurements, i.e. the cell $M_1|S|M_2|M'_1$ where the superscript indicates a difference in the electrical state. It is possible to write, in terms of the work to transport one electron from M_1 to M'_1:

$$eE = \bar{\mu}_e^{M'_1} - \bar{\mu}_e^{M_1} = e(\phi^{M_1} - \phi^{M'_1}) = e(\Delta_S^M\phi + \Delta_{M_2}^S\phi + \Delta_{M'_1}^{M_2}\phi) \tag{4}$$

Equation (4) readily defines E in terms of $\Delta\phi$ and no unambiguous splitting into two electrode potentials can be made in this form. From eqn. (4) the *operative electrode potential**, $\Delta_S^M\phi$, can be defined in terms of the *electrical* work to transport one electron *across the interface.* However, it is also possible to write:

$$eE = \Delta_{M_1}^{M'_1}\bar{\mu}_e = \Delta_{M_2}^{M'_1}\bar{\mu}_e + \Delta_S^{M_2}\bar{\mu}_e + \Delta_{M_1}^S\bar{\mu}_e \tag{5}$$

Since $\Delta_{M_1}^{M'_1}\bar{\mu}_e = 0$, eqn. (5) defines *unambiguously* two electrode potentials which are now independent of any metal—metal junction:

$$E = (-\Delta_S^{M_1}\bar{\mu}_e/e) - (-\Delta_S^{M_2}\bar{\mu}_e/e) \tag{6}$$

From a general point of view, the single *thermodynamic electrode potential* is defined in eqn. (6) in terms of the *electrochemical* (*chemical + electrical*) work to transport one electron *across the interface*. This definition corresponds exactly to the concept of electrode potential since it expresses the emission of electrons into the solution, so that the splitting involved in eqn. (6) is no longer disputable.

If eqn. (6) is treated in terms of eqns. (2) and (3), the definition of *absolute thermodynamic electrode potential* is now obtained as:

$$\epsilon_{abs}(M^+/M) = (\Delta_S^M\phi - \mu_e^M/e + \mu_e^S/e) \tag{7}$$

from which it results immediately that $k = \mu_e^S/e$. Since only the transfer of the unit charge is conceptually involved, μ_e^S may in fact be replaced by its standard value, $\mu_e^{0,S}$. The chemical potential of electrons in the solution corresponds to the energy of interaction of electrons with the structure of the solvent, i.e. the solvation energy of electrons. Now eqn. (7) corresponds to a really feasible

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* FD claim that this terminology is not justified from the historical point of view. However, they agree that $\Delta_S^M\phi$ was naturally called the absolute electrode potential as long as the concept of the potential drop at the interface between two different metals being zero was accepted. Now that we know that this is not the case, the terminology proposed here may be historically awkward but conceptually adequate. On the other hand, even though it is agreed that the only true electrode potential is $\Delta_S^M\phi$, the problem of understanding the physical meaning of the measured quantity E has still a profound conceptual sense, as shown by the number of misleading statements which can still be found in textbooks of electrochemistry (see ref. 2).

physical work and the potential is a truly absolute quantity. Like $\Delta_S^M\phi$, it pertains to one interface and as such it is not amenable of direct measurement. This contrasts apparently with the choice of k made by FD (their eqn. 7) on the basis of Kanevsky's [3] previous suggestion of $k = \chi^{S*}$. In fact, under such circumstances, ϵ_k does not pertain only to the metal/solution interface but to two interfaces simultaneously. For this reason ϵ_k is in fact a measurable quantity, but precisely for the same reason it cannot be defined as an electrode potential. The work implied in eqn. (2) when $k = \chi^S$ is in fact not a true physical work. Equation (2) with $k = \chi^S$ indicates that an electron is extracted from the metal, is passed through the metal—solution interface and finally is extracted from the solution and taken to infinity *under the condition that the solution phase is uncharged*. Thus, also ϵ_k is conditional if $k = \chi^S$, inasmuch as eqn. (2) would imply that $\psi^S = 0$. Alternatively, the electron can be left in the gas phase close to the solution surface**. However, physically, this is an artifact and in any case it corresponds to choosing ψ^S as the reference level, which is equivalent again to putting $\psi^S = 0$.

On the other hand, if $\psi^S \neq 0$ is accounted for in eqn. (2), then $k = \phi^S$ ($\Delta_0^S\phi$ in FD's notations) and ϵ_k would simply coincide with $\bar{\mu}_e^M$. Again, this is not the electrode potential for it does not explicitly involve the electrode—solution interface, although its value is governed by the nature of the solution in contact with the metal and it is an absolute quantity. In conclusion, the choice of k in eqn. (2) is not free, and now eqn. (7) defines the truly absolute thermodynamic electrode potential.

FD's comments are appreciated in that they throw light on some obscurities in the previous treatment. This discussion indicates that the reconsideration of these concepts in the electrochemical literature has not been unreasonable. Concepts of photoemission into solutions and physical meaning of electrode potential E have never explicitly been associated before. On the other hand, a practical problem where the knowledge of the absolute electrode potential (or at least of the potential ϵ_T) is not useless is the relationship between work func-

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* It is unclear why the condition that the surface potential of the solution is equal to zero is indicated by FD with $\Delta_0^S\phi = 0$, where subscript 0 stands for vacuum, i.e. by the Galvani potential at the vacuum (or air)—solution interface being equal to zero. In fact $\Delta_0^S\phi$ should be identical with χ^S only if $\psi^S = 0$, i.e. the solution phase is uncharged, which in the presence of metal—solution contact is *not* obvious.

** The identification of the point in the vacuum where the electron extracted from the metal should be located in the case of $k = 0$ (corresponding to ϵ_T) is unnecessary from a thermodynamic point of view. In fact, it is well known that in the equation $\epsilon_T = -\Delta G/e$ defining ϵ_T, ΔG is the change in *chemical* free energy for the reaction $M = M^+(S) + e$(vacuum). Thus, the position of e in the vacuum is irrelevant because $\mu_e = 0$ everywhere. Analogously, it is not necessary to assume a priori that $\chi^S = 0$. Both are *physical* consequences. In conclusion, eqn. (6) in FD's paper can be obtained without fixing the location of the electron. The work described by FD is the *real* work associated with the above reaction so that they give a physical and not a thermodynamic approach to ϵ_T. For this reason they need some model assumptions.

tions and potentials of zero charge [4]. It should be recalled that in the equation:

$$E^{\mathrm{M}}_{\sigma=0} = \Phi^{\mathrm{M}}/e - g^{\mathrm{S}}_{(\mathrm{M})}\,(\text{dipole}) - K \tag{8}$$

constant K is given by:

$$K = \epsilon^{0}_{\mathrm{T}}(\mathrm{H}^{+}/\mathrm{H}_2) - \delta\chi^{\mathrm{M}} \tag{9}$$

Equation (9) shows that in practical problems ϵ_{abs} does not appear because as we consider the work to transport one electron from the metal to the reference electrode through the solution, the particle is injected into and extracted from the solution in a way that the hydration energy of the electron appears twice with opposite signs in the equation. Thus, the relativity of the value of ϵ_{T} is in the fact that eqn. (1) implies that $\mu_{\mathrm{e}}^{0,\mathrm{S}} = 0$. On the other hand, the term 'conditional' used by FD for ϵ_{T} may be appropriate but the choice of possible other conditions is restricted to $k = 0$. ϵ_{T} is simply a not truly absolute electrode potential, although it is no longer a relative quantity because it is not measured with respect to another interface. Recalling eqn. (8), ϵ_{T} could be considered as the 'reduced' absolute electrode potential, although this definition may be a complication. On the other hand, this is the sole form of potential which can be obtained from an approach to the electrode process through a thermodynamic cycle like cycle (19) in the paper under discussion.

The surprising conclusion by FD that ϵ_{T} and ϵ_{k} may represent the chemical free solvation energy and the real free solvation energy, respectively, for electrons in the given solution ensues from the application of the quite new concept that metals are in electronic equilibrium with the *solution phase.* This approach leads to inacceptable consequences. Consider a metal in electronic equilibrium with the solution phase (viz. pure solvent). It results that:

$$\bar{\mu}^{\mathrm{M}}_{\mathrm{e}} = \bar{\mu}^{\mathrm{S}}_{\mathrm{e}} \tag{10}$$

from which:

$$\mu^{\mathrm{S}}_{\mathrm{e}} = \mu^{\mathrm{M}}_{\mathrm{e}} - e\Delta^{\mathrm{M}}_{\mathrm{S}}\phi \tag{11}$$

According to eqn. (1):

$$\mu^{\mathrm{S}}_{\mathrm{e}} = -\epsilon_{\mathrm{T}}(e_{\mathrm{S}}) \tag{12}$$

in agreement with FD's suggestion. Thus, according to eqn. (12) the experimental equilibrium potential of the electrode should correspond to the potential at which the light quantum energy for photoemission is zero. In fact, at this potential as implied in eqn. (10), the work to extract an electron from the metal is expected to vanish. Since the zero position for the extraction energy of electrons from the metal is now defined by eqn. (12), the *five-halves* *law* should be rewritten in the form [5,6]:

$$i_e = A\ \{h\nu - e[\epsilon_T - \epsilon_T(e_S)]\}^{5/2} \tag{13}$$

According to eqn. (13), at $\epsilon_T = \epsilon_T(e_S)$ $i_e = 0$ as $h\nu = 0$. At potentials more negative than $\epsilon_T(e_S)$ electrons are spontaneously emitted from the electrode. At potentials more positive than $\epsilon_T(e_S)$, an energy $h\nu$ is required for photoemission into the solution. Now, since $\epsilon_T(e_S)$ is expected from eqns. (10) to (12) to depend on the nature of the metal, at constant $h\nu$ the threshold potential for photoemission is predicted by eqn. (13) to be different for different metals. Thus, consideration of electronic equilibrium between electrode and solution phase leads to conclusions at variance with experimental findings [7,8].

Reconciliation of the above conclusions with the experimental situation is possible if it is considered that application of eqn. (13) to real systems requires constancy in $\epsilon_T(e_S)$ as ϵ_T is changed, i.e. the zero energy position is implied to remain the same. This would involve at any $\epsilon_T \neq \epsilon_T(e_S)$ a stationary flux of electrons through the interface from or to the electrode depending on the sign of the potential shift. This is conceivable only if electrons are really an intrinsic component of the solution. As a matter of fact, as ϵ_T is made anodic with respect to $\epsilon_T(e_S)$, electrons in solution (assuming the hypothesis of electronic equilibrium to hold) are injected into the electrode with a consequent change in μ_e^S and then in $\epsilon_T(e_S)$. The final point in solution will be the complete disappearance of electrons in solution so that eqn. (5) can now be correctly applied. This means that the condition of electronic equilibrium to describe ϵ_T or ϵ_k is unrealistic because this concept may be applied merely at the reversible potential for electrons in solution and may not be extended to any other potential inasmuch as departure from the equilibrium situation will lead exactly to the conditions for application of eqn. (5). Thus, FD's arguments have a very limited validity. On the contrary, eqn. (5) is applicable in a general way to any value of ϵ_T. To make a concrete example, Hg in contact with water at the potential of zero charge could be treated with eqn. (5) but certainly not with eqn. (10).

The concept of electronic equilibrium for metals in solution is also awkward in respect of present views on double layer structure. If electrons were present in solution, they would contribute to the solution charge whatever their concentration. Along these lines, the concept of ideally polarizable electrode [9] would be impossible and the Gibbs equation should contain an additional term for the surface excess of electrons in the solution. If in order to overcome this difficulty, electrical effects due to electrons in solution are supposed to be negligible, then it must be admitted that all equations developed so far for the double layer are in principle approximate. Conversely, if electrical effects are admittedly associated with electrons in solution, then this would imply that in double layer problems both potential profiles and charge balance in the solution should account for the presence of this new component. From all above it naturally ensues that conceptual difficulties also exist for the involvement of solvated electrons in electrode reactions [10].

Even though the conditions for electronic equilibrium were fulfilled, it is hard to realize the existence of a gradient of electron concentration within the bulk of the solution in a cell. FD's view apparently implies a sort of concentration cell where however, the cationic counterpart to establish a liquid junction potential is missing. Thus, electrodes are thought to be in electronic equilibrium with the solution whereas the latter is supposed not to be in electronic equilibrium in its own interior. This can hardly be reconciled with the well known high mobility and diffusivity of solvated electrons [11]. Further, if the concept of electronic equilibrium with the solution phase were accepted, the same potential ϵ_T for, say, Pt and Au in a solution containing the same redox couple could not be observed. In fact, μ_e^S should be the same to give the same ϵ_T, as eqn. (12) shows, for the two metals, but this would clearly be impossible because the two metals exhibit different work functions and they should emit different amounts of electrons to reach the equilibrium. The equilibrium potential between an electrode and a redox couple would thus be a mixed potential and should necessarily depend on the nature of the electrode since $\epsilon_T(e_S)$ does so. In any case, the idea should be accepted that a part of the potential drop in the double layer and a part of the charge in solution are due to electrons, which would take us very far. Conversely, if disappearance of electrons in solution is implied in ϵ_T made anodic with respect to $\epsilon_T(e_S)$, then the concept of mixed potential has nct to be introduced and any difficulty vanishes. Again, if this is the case, the conditions for application of eqn. (5) are unavoidably created.

It is true that in some solvents electrons may be present in the liquid phase at stable concentrations in equilibrium conditions. However, it is to be considered that for each electron in solution there is also a metal ion so that the equilibrium does not really refer to the following equation:

$$e(\mathrm{M}) \rightleftharpoons e(\mathrm{S}) \tag{14}$$

but rather to the more complex situation [12]:

$$\mathrm{M} \rightleftharpoons \mathrm{M}^+(\mathrm{S}) + e(\mathrm{S}) \tag{15}$$

which is a chemical and not an electrochemical equilibrium because it corresponds to the dissolution of the metal as neutral atoms.

That the electronic equilibrium of the metal with the solution is not relevant here is also implicit in concepts of Brodsky and Pleskov [13]. Their Fig. 9 clearly shows two different electronic energy levels, one for electrons in the metal which is of course the same for all metals at the same potential (same $\bar{\mu}_e^M$), and one for electrons in solution, quite distinct. If the metal were to be considered as in equilibrium with the solution, the Fermi level would be the same across the interface.

An electron may simply be used as a charge sample to measure the electronic energy in any point across a metal—solution interface. The potential drop along a metal wire may be defined in terms of the work associated with the transfer of an electron from one to the other end of the wire. Similarly, the potential ϵ of an electrode as usually measured may be defined in terms of the work associated with the transfer of an electron from a definite level in the metal (Fermi level) to a definite level in the solution (solvated electron). Since the chemical nature of the phases in contact is different, the work is not only electrical like in the case of the metal wire, hence the potential associated is not simply electrical. This is not a consequence of ϵ not being an electrode potential but rather of the procedure of measurement. A conclusion ensuing from all above is that the energy for extraction of electrons from a metal into the solution measures precisely $e\epsilon_{abs}$.

With reference to additional remarks on other works [14,15] of the present author, the paper by Frumkin et al. [16] came in fact to knowledge of the writer after he submitted his paper [14] for publication. However, this point becomes irrelevant as it is considered that the idea first [17] put forth for the Hg—Ga couple was already applied to other metals in the first paper [4] of this research line. In the same paper concepts were first touched regarding the possibility that $\chi^{H_2O} > g^{H_2O}_{(Hg)}$(dipole) and that $\delta\chi^M \neq 0$.

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