

Observable Electric Potential and Electrochemical Potentials

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The electric potential of the terminal of a reversible electrode is the observable electric potential (OEP) denoted by ψ . The local state in a differential element of an electrochemical system depends on its temperature, its pressure, its solute concentrations and its OEP. In the present work we are going to study the relationships between the electrochemical potentials and the OEP and discuss the possibilities of evaluating the electrochemical potentials profiles from measurements of spatial OEP distribution.

Our first example will be a system at thermodynamic equilibrium: a lead acid battery. A scheme of the battery and its electrochemical potentials profiles are given in Fig. 1. The profiles emphasize that the phases δ and β are barriers to the lead ions and to the electrons, respectively.

From Fig. 1 one can extract the condition which must be fulfilled in the translocation processes in cell membranes. The oxidation of NADH provides the energy for the proton transport. This process is reversible; nevertheless, until now nothing has been said about the characteristics and localization of the necessary protonic barrier inside the membrane.¹

In the field of nonequilibrium thermodynamics the OEP plays a central role; this quantity characterizes the observable formulation. The fluxes and driving forces are observable quantities in the OEP formulation.²⁻⁵

The formulation can be applied to different experimental conditions. We are going to focus in three cases: i) systems with concentration gradient; ii) systems with pressure gradient; and iii) systems with temperature gradient.

When we have concentration gradients as in liquid junctions the electrochemical profiles can be evaluated from measurements of the OEP as it is shown in Fig. 2.⁶ Also in systems with a pressure gradient, the electrochemical profiles can be calculated from OEP measurements; for the relaxation processes of streaming potential in membrane systems, shown in Fig. 3, a suggestive interpretation is given.⁷ Nevertheless, in systems with a temperature gradient, we cannot obtain the electrochemical profiles from OEP measurements.

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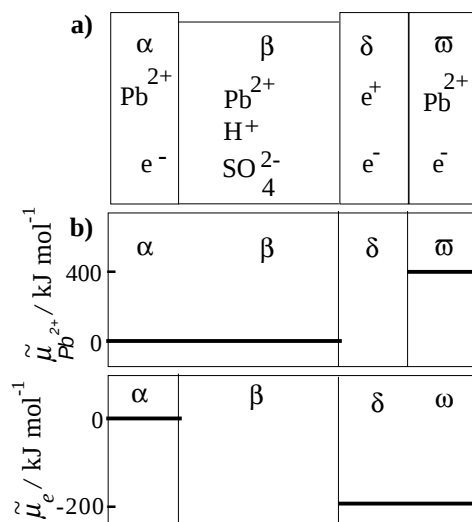


Fig. 1. Lead-acid battery: **a)** Phases and constituents with electric charge; α and ω are lead; δ is the lead oxide; and β is the liquid solution. The holes in the electronic semiconductor δ are denoted by e^+ . **b)** Electrochemical potential profiles.

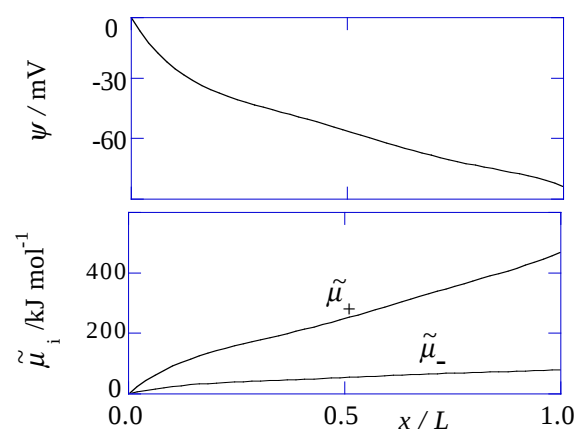


Fig. 2. OEP and electrochemical potentials profiles in the liquid junction $\text{H}_2\text{O}+\text{MgCl}_2$. We have a linear concentration profile: $c'=0.092 \text{ mol dm}^{-3}$ at $x=0$ and $c''=4.9 \text{ mol dm}^{-3}$ at $x=L$. The electric current is zero.⁶

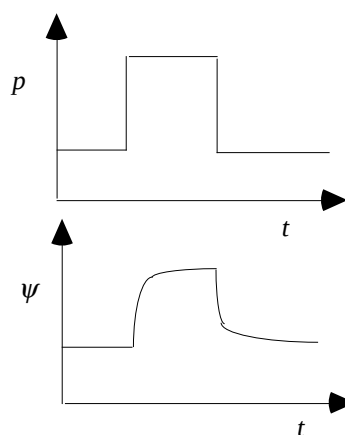


Fig. 3. When a squared pulse of pressure p is applied at a

