Chapter 14
Pseudo-reference Electrodes

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Both the terms of pseudo-reference (literally "false" reference) electrode and quasi-reference ("almost" or "essentially") electrode are used in the literature, often synonymously or interchangeably. The essential difference between a true reference electrode (as defined in Chap. 1) and a pseudo-reference electrode is the lack of thermodynamic equilibrium in the latter case [1–4]. In many cases simply platinum or silver or Ag/AgCl wires serve as pseudo- or quasi-reference electrodes. Obviously, thermodynamic equilibrium cannot exist, since there is no common component (anion or cation) in the two adjacent phases. However, usually they are calibrated by a reference redox system by adding the internal reference during the experiments into the electrolyte (preferred) or measuring their potential after the experiments by using a reference redox system or a conventional reference electrode. Sometimes when a reference redox system (e.g., ferrocene or cobaltocane) [5] is also used in situ, this reference electrode is called a quasi-reference electrode. These types of reference electrodes are used almost exclusively in nonaqueous systems (See Chaps. 2 and 6), in molten salts or at elevated temperatures, in ionic liquids (see Chap. 7), and mostly in three-electrode potentiostatic or potentiodynamic experiments. The advantages of the use of pseudo-reference electrodes are their simplicity, and because those are immersed directly into the electrolyte used in the cell, the ohmic resistance (impedance) effect is small, no liquid junction potential appears, and usually there is no contamination of the test solution by solvent molecules or ions that a conventional reference electrode might transfer. There are several disadvantages of the use of these reference electrodes. First is the lack of the thermodynamic equlibrium; therefore, one cannot calculate their potential. Second, because these are not ideally nonpolarizable electrodes, there is a shift of their potential during the measurements, which depends on the current density applied. Third, most pseudo-reference electrodes work over a limited range of conditions such as pH or temperature; outside of this

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range the electrodes' behavior becomes unpredictable. However, it should be mentioned that, although under suitably selected conditions the potential of the pseudo-reference electrode, although unknown, might be surprisingly constant during the experiments.

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