

Preface

One of the fundamental problems of the electrochemistry is that the Galvani potential difference across an interface, i.e., the difference of inner potentials of two adjacent phases, is not experimentally accessible. Consequently, the potential of a single electrode, i.e., a so-called half-cell consisting of one electron conductor and at least one ionic conductor cannot be determined. By combining two electrodes to a complete galvanic cell or electrolytic cell, potential difference between the two metallic terminals can be measured. The two metallic terminals should be identical for any meaningful potential measurement, and under certain conditions the measured potential is characteristic to the electrode potential intended to determine. For this purpose we use reference electrodes. Reference electrodes are galvanic half-cells which are designed to provide a stable and reproducible Galvani potential difference, either as a primary standard (the standard hydrogen electrode) or as secondary standards. In order to produce reliable experimental data, reference electrodes have to fulfill many, partly contradictory conditions, which practically never can be met to full satisfaction. For the choice and application of a particular reference electrode it is of utmost importance to know its properties as detailed as possible.

It is of great theoretical interest to relate a Galvani potential difference to the absolute potential of a clearly defined species, e.g., the potential of a free electron in vacuum. This defines an absolute potential scale (see Chap. 15), for which the *precise* relation to the conventional standard hydrogen electrode scale for aqueous solutions is still debated. Hence, a consistent system based on the standard hydrogen electrode (SHE) definition still serves the fundamental needs of measuring and calculating redox equilibria, and coupled chemical equilibria in aqueous systems. The relation of the electrode potentials in nonaqueous systems, be they liquid or solid, to the (aqueous) SHE, is of fundamental importance in chemistry because nonaqueous systems play an important role in modern technologies and research, and in many cases aqueous and nonaqueous systems are even directly coupled, as, e.g., in ion partition systems.

Therefore, the authors of this *Handbook of Reference Electrodes* were guided by the idea to provide all necessary and reliable data. The last and only handbook on

reference electrodes was published in 1961 [Ives DJG, Janz GJ (1961) Reference electrodes. Theory and practice. Academic, New York]. Although the progress in this field of research and technology was rather steady and not revolutionary in the last half century, a lot of information vital for modern electrochemistry has been added during that time. Naturally, the Ives/Janz book could not contain information on reference electrodes for solid-state electrolyte systems and nothing about room temperature ionic liquids, glass melts, reference electrodes based on conducting polymers, etc., since these topics strongly developed in the last decades.

In the first section this handbook provides the fundamentals of thermodynamics and kinetics of reference electrodes, and then liquid junction potentials and salt bridges are discussed, as they are involved in almost all reference systems. The following chapters present the various reference electrodes and systems as they are presently used. A final chapter is devoted to the Kelvin probe and discusses this instrument as a reference electrode for contact potential measurements.

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