

CHAPTER OVERVIEW

14: Galvanic Cells

An *electrochemical cell* is a system in which passage of an electric current through an electrical circuit is linked to an internal cell reaction. A **galvanic cell**, or voltaic cell, is an electrochemical cell that, when isolated, has an electric potential difference between its terminals; the cell is said to be a *seat of electromotive force*.

The cell reaction in a galvanic cell differs in a fundamental way from the same reaction (i.e., one with the same reaction equation) taking place in a reaction vessel that is not part of an electrical circuit. In the reaction vessel, the reactants and products are in the same phase or in phases in contact with one another, and the reaction advances in the spontaneous direction until reaction equilibrium is reached. This reaction is the *direct reaction*.

The galvanic cell, in contrast, is arranged with the reactants physically separated from one another so that the cell reaction can advance only when an electric current passes through the cell. If there is no current, the cell reaction is constrained from taking place. When the electrical circuit is open and the cell is isolated from its surroundings, a state of thermal, mechanical, and transfer equilibrium is rapidly reached. In this state of *cell equilibrium* or *electrochemical equilibrium*, however, reaction equilibrium is not necessarily present—that is, if the reactants and products were moved to a reaction vessel at the same activities, there might be spontaneous advancement of the reaction.

As will be shown, measurements of the cell potential of a galvanic cell are capable of yielding precise values of molar reaction quantities of the cell reaction and thermodynamic equilibrium constants, and of mean ionic activity coefficients in electrolyte solutions.

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