

17.12: Standard Electrode Potentials

We adopt a very useful convention to tabulate the potential drops across standard electrochemical cells, in which one half-cell is the S.H.E. Since the potential of the S.H.E. is zero, we define the **standard electrode potential**, \mathcal{E}^o , of any other standard half-cell (and its associated half-reaction) to be the potential difference when the half-cell operates spontaneously versus the S.H.E. The electrical potential of the standard half-cell determines both the magnitude and sign of the standard half-cell potential.

If the process that occurs in the half-cell reduces a solution species or the electrode material, electrons traverse the external circuit toward the half-cell. Hence, the electrical sign of the half-cell terminal is positive. By the convention, the algebraic sign of the cell potential is positive ($\mathcal{E}^o > 0$). If the process that occurs in the half-cell oxidizes a solution species or the electrode, electrons traverse the external circuit away from the half-cell and toward the S.H.E. The electrical sign of the half-cell is negative, and the algebraic sign of the cell potential is negative ($\mathcal{E}^o < 0$).

If we know the standard half-cell potential, we know the essential electrical properties of the standard half-cell operating spontaneously versus the S.H.E. at zero current. In particular, the algebraic sign of the standard half-cell potential tells us the direction of current flow and hence the direction of the reaction that occurs spontaneously.

An older convention associates the sign of the standard electrode potential with the direction in which an associated half-reaction is written. This convention is compatible with the definition we have chosen; however, it creates two ways of expressing the same information. The difference is whether we write the direction of the half-reaction with the electrons appearing on the right or on the left side of the equation.

When the half-reaction is written as a reduction process, with the electrons appearing on the left, the associated half-cell potential is called the **reduction potential** of the half-cell. Thus we would convey the information we have developed about the silver–silver ion and the copper–copper ion half cells by presenting the reactions and their associated potentials as

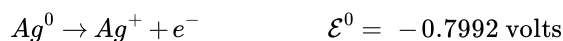


When the half-reaction is written as a reduction process, the sign of the electrode potential is the same as the sign of the electrical potential of the half-cell when the half-cell operates spontaneously versus the S.H.E. Thus, the reduction potential has the same algebraic sign as the electrode potential of our definition.

We can convey the same information by writing the half-reaction in the reverse direction; that is, as an oxidation process in the left-to-right direction so that the electrons appear on the right. The agreed-upon convention is that we reverse the sign of the half-cell potential when we reverse the direction in which we write the equation. When the half-reaction is written as an oxidation process, the associated half-cell potential is called the **oxidation potential** of the half-cell. Older tabulations of electrochemical data often present half-reactions written as oxidation processes, with the electrons on the right, and present the potential information using the oxidation potential convention.



reduction potential

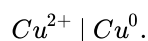


oxidation potential

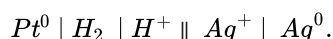
Note that, in the convention that we have adopted, the term half-cell potential always denotes the potential of the half-cell when it operates spontaneously versus the S.H.E. In this convention, we do not need to write the half-reaction in order to specify the standard potential. It is sufficient to specify the chemical constituents of the half-cell. This is achieved using another representational convention.

Cell Notation

This cell-describing convention lists the active components of a half-cell, using a vertical line to indicate the presence of a phase boundary like that separating silver metal from an aqueous solution containing silver ion. The silver–silver ion cell is denoted $\text{Ag}^+ | \text{Ag}^0$. (Using the superscript zero on the symbol for elemental silver is redundant; however, it does promote clarity.) The copper–cupric ion cell is denoted



The S.H.E. is denoted $H^+ | H_2 | Pt^0$, reflecting the presence of three distinct phases in the operating electrode. A complete electrochemical cell can be described using this convention. When the complete cell contains a salt bridge, this is indicated with a pair of vertical lines||. A cell composed of a silver–silver ion half-cell and a S.H.E. is denoted



A further convention stipulates that the half-cell with the more positive electrode potential is written on the right. Under this convention, spontaneous operation of the standard full cell transfers electrons through the external circuit from the terminal shown on the left to the terminal shown on the right.

We can now present our information about the behavior of the silver–silver ion half-cell versus the S.H.E. by writing that the standard potential of the $Ag^+ | Ag^0$ half-cell is +0.7792 volts. The standard potential of the $Cu^{2+} | Cu^0$ half-cell is +0.3394 volts. The standard potential of the $H^+ | H_2 | Pt^0$ (the S.H.E.) half-cell is 0.0000 volts. Again, our definition of the standard electrode potential makes the sign of the standard electrode potential independent of the direction in which the equation of the corresponding half-reaction is written.

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