14.6: Standard Electrode Potentials

Section 14.5 explained how, by measuring the equilibrium cell potential of a galvanic cell at different electrolyte molalities, we can evaluate the standard cell potential $E^\circ_{\text{cell, eq}}$ of the cell reaction. It is not necessary to carry out this involved experimental procedure for each individual cell reaction of interest. Instead, we can calculate $E^\circ_{\text{cell, eq}}$ from standard electrode potentials.

By convention, standard electrode potentials use a standard hydrogen electrode as a reference electrode. A **standard hydrogen electrode** is a hydrogen electrode, such as the electrode shown at the left in Fig. 14.1, in which the species $H_2(g)$ and $H^+(aq)$ are in their standard states. Since these are *hypothetical* gas and solute standard states, the standard hydrogen electrode is a hypothetical electrode—not one we can actually construct in the laboratory.

A **standard electrode potential** E° is defined as the standard cell potential of a cell with a hydrogen electrode at the left and the electrode of interest at the right. For example, the cell in Fig. 14.1 with cell diagram

$$\mathrm{Pt}\,|\,\mathrm{H_2(g)}\,|\,\mathrm{HCl(aq)}\,|\,\mathrm{AgCl(s)}\,|\,\mathrm{Ag}$$

has a hydrogen electrode at the left and a silver–silver chloride electrode at the right. The standard electrode potential of the silver–silver chloride electrode, therefore, is equal to the standard cell potential of this cell.

Since a cell with hydrogen electrodes at both the left and right has a standard cell potential of zero, the standard electrode potential of the hydrogen electrode is *zero* at all temperatures. The standard electrode potential of any other electrode is nonzero and is a function only of temperature.

Consider the following three cells constructed from various combinations of three different electrodes: a hydrogen electrode, and two electrodes denoted L and R.

- We wish to calculate the standard cell potential $E^\circ_{\text{cell, eq}}$ of cell 1 from the standard electrode potentials E°_{L} and E°_{R}.

  If we write the cell reactions of cells 1 and 2 using the same value of the electron number z for both, we find that their sum is the cell reaction for cell 3 with the same value of z. Call these reactions 1, 2, and 3, respectively:

  $$(\text{reaction } 1) + (\text{reaction } 2) = (\text{reaction } 3) \tag{14.6.1}$$

  Equation 14.6.3 is a general relation applicable to any galvanic cell. It should be apparent that we can use the relation to calculate the standard electrode potential of an electrode from the standard electrode potential of a different electrode and the standard cell potential of a cell that contains both electrodes. Neither electrode has to be a hydrogen electrode, which is difficult to work with experimentally.

  Using Eq. 14.6.3 to calculate standard cell potentials from standard electrode potentials saves a lot of experimental work. For example, measurement of $E^\circ_{\text{cell, eq}}$ for ten different cells, only one of which needs to include a hydrogen electrode, provides values of E° for ten electrodes other than E°=0 for the hydrogen electrode. From these ten values of E°, values of $E^\circ_{\text{cell, eq}}$ can be calculated for 35 other cells without hydrogen electrodes.