17.6: Electrochemical Cells as Circuit Elements

Suppose we use a wire to connect the terminals of the cell built from the silver–silver ion half-cell and the copper–cupric ion half-cell. This wire then constitutes the external circuit, the path that the electrons follow as chemical change occurs within the cell. When the external circuit is simply a low-resistance wire, the cell is short-circuited. The external circuit can be more complex. For example, when we want to know the direction of electron flow, we incorporate a galvanometer.

If the reaction between silver ions and copper metal is to occur, electrons must pass through the external circuit from the copper terminal to the silver terminal. An electron that is free to move in the presence of an electrical potential must move away from a region of more negative electrical potential and toward a region of more positive electrical potential. Since the electron-flow is away from the copper terminal and toward the silver terminal, the copper terminal must be electrically negative and the silver terminal must be electrically positive. Evidently, if we know the chemical reaction that occurs in an electrical cell, we can immediately deduce the direction of electron flow in the external circuit. Knowing the direction of electron flow in the external circuit immediately tells us which is the negative and which the positive terminal of the cell.

The converse is also true. If we know which cell terminal is positive, we know that electrons in the external circuit flow toward this terminal. Even if we know nothing about the composition of the cell, the fact that electrons are flowing toward a particular terminal tells us that the reaction occurring in that half-cell is one in which a solution species, or the electrode material, takes up electrons. That is to say, some chemical entity is reduced in a half-cell whose potential is positive. It can happen that we know the half-reaction that occurs in a given half-cell, but that we do not know which direction the reaction goes. For example, if we replace the silver–silver ion half cell with a similar cell containing an aqueous zinc nitrate solution and a zinc electrode, we are confident that the half-cell reaction is either

$$\mathrm{Zn}^0 \rightarrow \mathrm{Zn}^{2+} + 2\,\mathrm{e}^-$$

or

$$\mathrm{Zn}^{2+} + 2\,\mathrm{e}^- \rightarrow \mathrm{Zn}^0$$

When we determine experimentally that the copper electrode is electrically positive with respect to the zinc electrode, we know that electrons are leaving the zinc electrode and flowing to the copper electrode. Therefore, the cell reaction must be

$$\mathrm{Zn}^0 + \mathrm{Cu}^{2+} \rightarrow \mathrm{Zn}^{2+} + \mathrm{Cu}^0$$

It is convenient to have names for the terminals of an electrochemical cell. One naming convention is to call one terminal the ***anode*** and the other terminal the ***cathode***. The definition is that the cathode is the electrode at which a reacting species is reduced. In the silver–silver ion containing cell, the silver electrode is the cathode. In the zinc–zinc ion containing cell, the copper electrode is the cathode. In these cells, the cathode is the electrically positive electrode. An important feature of these experiments is that the direction of the electrical potential in the external circuit is established by the reactions that occur spontaneously in the cells. The cells are sources of electrical current. Cells that operate to produce current are called ***galvanic*** cells.