14.1: Cell Diagrams and Cell Reactions

14.1.1 Elements of a galvanic cell

We will treat a galvanic cell as a *system*. The cell has two metal wires called *terminals* that pass through the system boundary. Within the cell are phases that can conduct an electric current and are collectively called *electrical conductors*. Each terminal is attached to an *electron conductor* that is usually a metal, but might also be graphite or a semiconductor. Each electron conductor is in contact with an *ionic conductor*, usually an electrolyte solution, through which ions but not electrons can move. Both of the electron conductors can be in contact with the same ionic conductor; or they can be in contact with separate ionic conductors, in which case the ionic conductors contact one another at a *liquid junction*. The general arrangement of the physical elements of a galvanic cell is therefore

$$\text{terminal} - \text{electron conductor} - \text{ionic conductor(s)} - \text{electron conductor} - \text{terminal} \tag{14.1.1}$$

Both terminals must be the same metal (usually copper) in order for it to be possible to measure the electric potential difference between them.

The combination of an electron conductor and the ionic conductor in contact with it is called an **electrode**, or half-cell. (The term “electrode” is sometimes used to refer to just the electron conductor.) To describe a galvanic cell, it is conventional to distinguish the *left* and *right* electrodes. In this way, we establish a left–right association with the reactants and products of the reactions at the electrodes.

14.1.2 Cell diagrams

The cell of Fig. 14.1 has a single electrolyte phase with essentially the same composition at both electrodes, and is an example of a *cell without liquid junction* or *cell without transference*. As an example of a *cell with transference*, consider the cell diagram

$$\mathrm{Zn} \mid \mathrm{Zn}_2^+(\mathrm{aq}) \,\vdots\, \mathrm{Cu}_2^+(\mathrm{aq}) \mid \mathrm{Cu} \tag{14.1.2}$$

This is the zinc–copper cell depicted in Fig. 14.2, sometimes called a Daniell cell. The two electrolyte phases are separated by a liquid junction represented in the cell diagram by the dashed vertical bar. If the liquid junction potential can be assumed to be negligible, the liquid junction is instead represented by a pair of dashed vertical bars:

$$\mathrm{Zn} \mid \mathrm{Zn}_2^+(\mathrm{aq}) \,\vdots\vdots\, \mathrm{Cu}_2^+(\mathrm{aq}) \mid \mathrm{Cu}$$

14.1.4 Advancement and charge

The **electron number** or charge number, z, of the cell reaction is defined as the amount of electrons entering at the right terminal per unit advancement of the cell reaction. z is a positive dimensionless quantity equal to $|\nu_\mathrm{e}|$, where ν_e is the stoichiometric number of the electrons in either of the electrode reactions whose sum is the cell reaction.

Because both electrode reactions are written with the same value of $|\nu_\mathrm{e}|$, the advancements of these reactions and of the cell reaction are all described by the same advancement variable ξ. For an infinitesimal change $\mathrm{d}\xi$, an amount of electrons equal to $z\,\mathrm{d}\xi$ enters the system at the right terminal, an equal amount of electrons leaves at the left terminal, and there is no buildup of charge in any of the internal phases.

The **Faraday constant** F is a physical constant defined as the charge per amount of protons, and is equal to the product of the elementary charge (the charge of a proton) and the Avogadro constant: $F = eN_\mathrm{A}$. Its value to five significant figures is $F = 96,485\ \mathrm{C\ mol^{-1}}$. The charge per amount of electrons is $-F$. Thus, the charge entering the right terminal during advancement $\mathrm{d}\xi$ is

$$\mathrm{đ}Q_\mathrm{sys} = -zF\,\mathrm{d}\xi \tag{14.1.1}$$