12.10: Charging a Battery

The concept of "non-*PdV* work" sometimes causes difficulty, so am going to illustrate it in this section by using the charging of a battery as an example, and in the next section by a discussion of surface tension. This section will also give us an opportunity of using a Gibbs-Helmholtz relation.

Suppose that we force a charge q into an electric cell whose electromotive force (EMF) is E, at constant temperature and pressure. What is the increase in the Gibbs function of the cell? And what is the increase in its enthalpy?

The answer to the first question is easy. It is just qE. The increase in the enthalpy is given by

$$\Delta H = \Delta G + T\Delta S$$

and, by a Maxwell relation (equation 12.6.12a), this is

$$\Delta H = \Delta G - T\Delta\left(\frac{\partial G}{\partial T}\right)_P, \tag{12.10.1}$$

which is one of the Gibbs-Helmholtz relations. But since ΔG = qE, this becomes

$$\Delta H = q\mathcal{E} - Tq\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P = q\left[\mathcal{E} - T\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P\right]. \tag{12.10.2}$$

Thus we can calculate the increase in enthalpy from a measurement of how the EMF of the cell changes with temperature.