17.5: Electrical Potential

Electrical potential is measured in volts. If a system comprising one coulomb of charge passes through a potential difference of one volt, one joule of work is done on the system. The work done on the system is equal to the change in the energy of the system. For Q coulombs passing through a potential difference of $\mathcal{E}$ volts, we have $\Delta E = w_{elec} = Q\mathcal{E}$. Whether this represents an increase or a decrease in the energy of the system depends on the sign of the charge and on the sign of the potential difference.

Electrical potential and gravitational potential are analogous. The energy change associated with moving a mass from one elevation to another in the earth's gravitational field is

$$\Delta E = w_{grav} = mgh_{final} - mgh_{initial} = m\mathit{\Phi}_{grav}$$

where $\mathit{\Phi}_{grav} = g\left(h_{final} - h_{initial}\right)$, which is the gravitational potential difference.

The role played by charge in the electrical case is played by mass in the gravitational case. The energies of these systems change because charge or mass moves in response to the application of a force. In the electrical case, the force is the electrical force that arises from the interaction between charges. In the gravitational case, the force is the gravitational force that arises from the interaction between masses. A notable difference is that mass is always a positive quantity, whereas charge can be positive or negative.

The distinguishing feature of an electrochemical cell is that there is an electrical potential difference between the two terminals. For any given cell, the magnitude of the potential difference depends on the magnitude of the current that is flowing. (Making the general problem even more challenging, we find that it depends also on the detailed history of the conditions under which electrical current has been drawn from the cell.) Fortunately, if we keep the cell's temperature constant and measure the potential at zero current, the electrical potential is constant. Under these conditions, the cell's characteristics are fixed, and potential measurements give reproducible results. We want to understand the origin and magnitude of this potential difference. Experimentally, we find:

1. If we measure the zero-current electrical potential of the same cell at different temperatures, we find that this potential depends on temperature.
2. If we prepare two cells with different chemical species, they exhibit different electrical potentials—except possibly for an occasional coincidence.
3. If we prepare two cells with the same chemical species at different concentrations and measure their zero-current electrical potentials at the same temperature, we find that they exhibit different potentials.
4. If we draw current from a given cell over a period of time, we find that there is a change in the relative amounts of the reagents present in the cell. Overall, a chemical reaction occurs; some reagents are consumed, while others are produced.

We can summarize these experimental observations by saying that the central issue in electrochemistry is the interrelation of three characteristics of an electrochemical cell: the electrical-potential difference between the terminals of the cell, the flow of electrons in the external circuit, and the chemical changes inside the cell that accompany this electron flow.

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