
Electrochemistry

17.1 What is electrochemistry?

- Electrochemistry involves the interconversion of electrical energy and chemical energy.
- Charge can be moved by electron transfer through conductors and by ion transport in solutions.
- The maximum voltage produced by an electrochemical cell is called the zero-current cell potential, E_{cell} . It is also known as the electromotive force, emf.
- Redox reactions involve simultaneous reduction and oxidation half reactions.
 - **Reductions** involve **gain** of electrons.
 - **Oxidations** involve **loss** of electrons.

17.2 Ions in solution

- Electrolytes are substances that dissolve to give conducting solutions, usually due to the movement of ions.
- The conductivity, κ , measures how easily charge is transported through a solution.
- The molar conductivity of a compound, Λ_{m} , is given by κ/c , where c is the concentration of the solution in mol m^{-3} .
- The ionic conductivity, λ , is characteristic of an individual ion and independent of the other ions present.
- For a strong electrolyte, Λ_{m} increases with dilution, up to a value at infinite dilution called the limiting molar conductivity, $\Lambda_{\text{m}}^{\circ}$.
- For a weak electrolyte, the conductivity is largely influenced by the degree of ionization.

- The conductivities of hydrogen ions and hydroxyl ions are high due to the Grotthus mechanism.
- For any electrolyte, $\Lambda_m^\circ = \nu_+\lambda_+ + \nu_-\lambda_-$, where ν_+ and ν_- are the numbers of cations and anions formed when one formula unit of the electrolyte dissolves.

17.3 Electrochemical cells

- Electrochemical cells involve reduction and oxidation reactions arranged so that electrons can flow through an external circuit.
- A cell consists of two half reactions. **Reduction** occurs at the **cathode**; **oxidation** occurs at the **anode**.
- A cell diagram is a convenient way of representing an electrochemical cell on paper (see Figure 17.10).

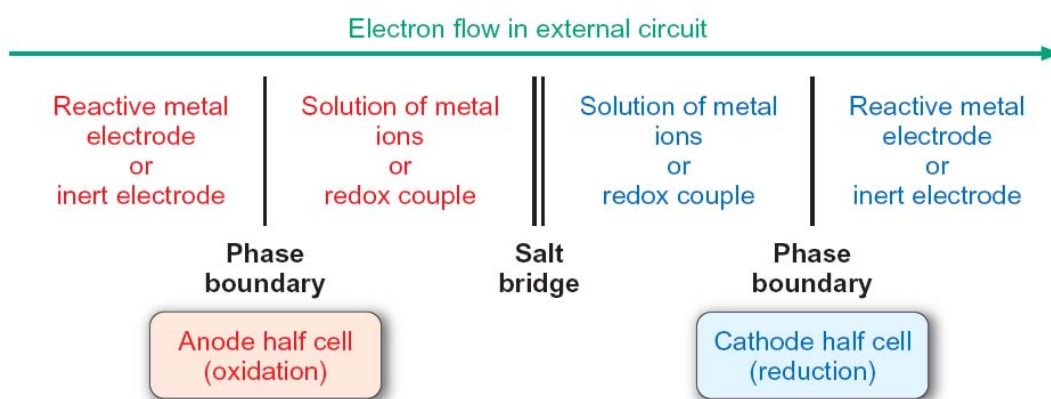


Figure 17.10 A generalized cell diagram to represent an electrochemical cell.

- The standard hydrogen electrode is a half cell in which hydrogen gas is bubbled over a platinum foil immersed in a solution of H^+ (aq) (see Figure 17.8). It is assigned a potential of $E^\ominus = 0.00 \text{ V}$ under standard conditions of 298.15 K (25 °C), hydrogen gas pressure of 1.00 bar, and H^+ (aq) activity = 1.

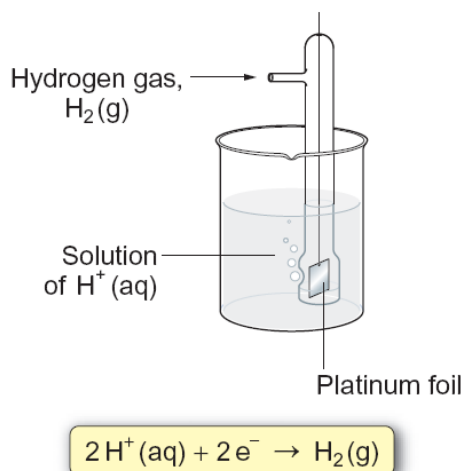


Figure 17.8 Hydrogen electrode.

- The standard reduction potential, E^\ominus , is the potential of a reduction half cell relative to the standard hydrogen electrode set to $E^\ominus = 0.00 \text{ V}$ with all species in their standard states.
- Under standard conditions, a half reaction with a high (positive) E^\ominus will oxidize a half reaction with lower (less positive) E^\ominus .

The overall cell potential (emf) is given by

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}}$$

- A list of half reactions ordered in terms of E^\ominus and oxidizing power is known as the electrochemical series.

17.4 Thermodynamics of electrochemical cells

- E^\ominus_{cell} is related to the standard Gibbs energy change for the reaction by

$$\Delta_{\text{r}}G^\ominus = -zFE^\ominus_{\text{cell}}$$

- E^\ominus_{cell} is related to the thermodynamic equilibrium constant by

$$E^\ominus_{\text{cell}} = \frac{RT}{zF} \ln K$$

- A positive value of E_{cell} indicates that the cell reaction will be spontaneous in the forward direction.
- The variation in cell potential with changing concentration of the cell contents is given by the Nernst equation

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{zF} \ln Q$$

- A concentration cell comprises two half cells that are identical apart from the concentration of the ion.

17.5 Electrolysis

- Electrolysis reactions involve using electrical power to drive non-spontaneous reactions.
- Electrolysis has important applications, including the manufacture of metals, chlorine, sodium hydroxide, and hydrogen. It is also used in the charging cycle of rechargeable batteries.
- The cell reaction in a primary cell is not reversible, so batteries using primary cells cannot be recharged.
- Secondary cells employ reversible reactions and can be recharged.

Learning outcomes

By the end of this chapter you should be able to do the following.

- Describe, and give examples of, the uses of electrochemical reactions.
- Define conductivity and molar conductivity for a solution of an electrolyte and explain how the molar conductivity of a strong electrolyte depends on concentration.
- Calculate the limiting molar conductivity of a strong electrolyte from the individual ionic conductivities of the cations and anions present.
- Understand that an electrochemical cell is made up of two half cells; reduction occurs at the cathode and oxidation at the anode.
- Construct and use cell diagrams.
- Define the standard reduction potential, E^{\ominus} , and use it to calculate $E^{\ominus}_{\text{cell}}$.
- Use $E^{\ominus}_{\text{cell}}$ to predict the spontaneity of a redox reaction.
- Use $E^{\ominus}_{\text{cell}}$ data to calculate $\Delta_r G^{\ominus}$ and K , and vice versa.

- Use the Nernst equation to calculate the cell potential, E_{cell} , under non-standard conditions.
- Explain what is meant by a concentration cell.
- Describe the basic principles of electrolysis and how it is used in chemical processes.
- Give some examples of primary and secondary batteries and their underlying electrochemistry.