16

Electrochemistry

16.1   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.

16.2   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 $mol\,m^{-3}$.

- For a strong electrolyte, Λ_m increases with dilution, up to a value at infinite dilution called the limiting molar conductivity, Λ_m°.

- For a weak electrolyte, the conductivity is largely influenced by the degree of ionization.

- The ionic conductivity, λ, is characteristic of an individual ion and independent of the other ions present.

- The conductivities of H^+ ions and OH^- ions are high due to the Grotthus mechanism.

- For any electrolyte, $\Lambda_m^\circ = v_+\lambda_+ + v_-\lambda_-$, where v_+ and v_- are the numbers of cations and anions formed when one formula unit of the electrolyte dissolves.

- ? For practice questions on these topics, see questions 1 and 2 at the end of this chapter (p.761).

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16.3   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 16.10, p.739).

- 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 16.8, p.737). It is assigned a potential of $E^{\ominus} = 0.00\,V$ under standard conditions of 298 K (25 °C), hydrogen gas pressure of 1.00 bar, and $H^+(aq)$ concentration = $1\,mol\,dm^{-3}$.

- The standard reduction potential, $E^{\ominus}$, is the potential of a reduction half cell relative to the standard hydrogen electrode set to $E^{\ominus} = 0.00\,V$ 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

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$$

- A list of half reactions ordered by value of $E^{\ominus}$ and oxidizing power is known as the electrochemical series.

? For practice questions on these topics, see questions 3–11 at the end of this chapter (pp.761–762).

16.4   Thermodynamics of electrochemical cells

- The Faraday constant F is the charge on 1 mol of electrons and has a value of 96 485 coulombs.

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

$$\Delta_r G^{\ominus} = -zFE^{\ominus}_{cell}$$

- $E^{\ominus}_{cell}$ is related to the thermodynamic equilibrium constant by

$$E^{\ominus}_{cell} = \frac{RT}{zF}\ln K$$

- 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

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

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

? For practice questions on these topics, see questions 12–16 at the end of this chapter (p.762).

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16.5 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.

- Reacting quantities in electrolytic reactions can be calculated using the Faraday constant.

- 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.

? For practice questions on these topics, see questions 17–19 at the end of this chapter (p.762).

» Concept review

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 $E^{\ominus}_{cell}$.

- Use $E^{\ominus}_{cell}$ to predict the spontaneity of a redox reaction.

- Use $E^{\ominus}_{cell}$ 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.

- Use the Faraday constant to calculate reacting quantities in electrolytic reactions.

- Give some examples of primary and secondary cells and their underlying electrochemistry.

⇄ Key equations

Law of independent migration of ions	$\Lambda^{\circ}_m = v_+\lambda_+ + v_-\lambda_-$	(16.8)
Calculation of $E^{\ominus}$ for a cell	$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$	(16.10)
The Faraday constant	$F = $ charge on 1 mol of electrons $= 96\,485\,C\,mol^{-1}$	(16.12)
Gibbs energy change and $E^{\ominus}$ for a cell	$\Delta_r G^{\ominus} = -zF \times E^{\ominus}_{cell}$	(16.14)
Equilibrium constant and $E^{\ominus}$ for a cell	$\ln k = \dfrac{zF}{RT}E^{\ominus}_{cell}$	(16.15)
The Nernst equation	$E^{\ominus}_{cell} = E^{\ominus}_{cell} - \dfrac{RT}{zF}\ln Q$	(16.16)
	$E^{\ominus}_{half\,cell} = E^{\ominus}_{half\,cell} - \dfrac{RT}{zF}\ln Q$	(16.17)
Membrane potential	$\Delta E_{M^+} = \dfrac{RT}{zF}\ln\dfrac{[M^+]_{outside}}{[M^+]_{inside}}$	(16.18)

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