

Equilibrium Electrochemistry

Introduction

Electrochemistry is the study of processes that involve the transfer of electrons, specifically the interconversion between chemical energy and electrical energy. This field is fundamentally governed by the principles of equilibrium and thermodynamics, allowing us to predict and quantify the potential difference generated by a redox reaction.

This module focuses on quantifying cell potential and using electrochemical methods to measure thermodynamic properties like the equilibrium constant and pH:

- We will define the components of an electrochemical cell and use standard potentials to determine spontaneity.
- We will apply the Nernst equation to understand how concentration affects the cell potential.

Learning Objectives

By the end of this module, you will be able to:

- **Discuss and construct** a diagram of the structure of electrochemical cells (galvanic and electrolytic).
- **Decide** through calculations whether a cell will generate electric current spontaneously.
- **Describe and apply** through calculations on concentration cells with and without transference.
- **Apply** electrochemical principles for the measurement of pH, equilibrium constants, and potentiometric titrations.

Key Concepts and Definitions

Term	Definition
Electrochemical Cell	A device that converts chemical energy into electrical energy (galvanic) or vice versa (electrolytic).
Galvanic (Voltaic) Cell	An electrochemical cell where a spontaneous redox reaction ($\Delta G < 0$) produces electric current.
Standard Electrode Potential (E°)	The potential of a half-cell relative to the Standard Hydrogen Electrode (SHE , $E^\circ = 0.00 \text{ V}$) under standard conditions.
Cell Potential (E_{cell})	The electromotive force (EMF) generated by the cell, measured in Volts (V). Positive E_{cell} indicates spontaneity.
Nernst Equation	An equation that relates the cell potential to standard potential and reaction quotient (Q) under non-standard conditions.
Concentration Cell	A galvanic cell constructed using the same electrode and electrolyte in both half-cells, but at different concentrations. The driving force is the difference in concentration.

Detailed Discussion

1. Structure and Spontaneity of Electrochemical Cells

An electrochemical cell is composed of two half-cells: the **anode** (where oxidation occurs) and the **cathode** (where reduction occurs). They are connected by an external circuit and an internal salt bridge.

The driving force of a galvanic cell is the potential difference, quantified by the **Standard Cell Potential (E°_{cell})**.

Standard Cell Potential :

$$E^\circ_{cell} = E^\circ_{reduction \text{ (cathode)}} - E^\circ_{reduction \text{ (anode)}}$$

- **Spontaneity Criterion:** If $E^\circ_{cell} > 0$, the reaction is spontaneous and can generate power (galvanic cell). If $E^\circ_{cell} < 0$, the reaction is non-spontaneous and requires an external power source (electrolytic cell).

2. Relationship between ΔG and E_{cell}

The thermodynamic spontaneity criterion (ΔG) is directly linked to the electrical potential (E_{cell}). This fundamental relationship is used to quantify the maximum electrical work a cell can perform.

Gibbs Free Energy and Cell Potential :

$$\Delta G = -nFE_{cell}$$

Where n is the number of moles of electrons transferred, and F is Faraday's constant (**96,485 C/mol e⁻**).

3. The Nernst Equation and Non-Standard Conditions

The **Nernst Equation** is used to calculate the actual cell potential (E_{cell}) when concentrations or pressures are not at the standard 1 M or 1 atm. It incorporates the reaction quotient (Q), which measures how far the system is from equilibrium:

Nernst Equation (General Form):

$$E_{cell} = E^{\circ}_{cell} - (R T / n F) \ln Q$$

Nernst Equation (Simplified at 298 K):

$$E_{cell} = E^{\circ}_{cell} - (0.0592 V / n) \log Q$$

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4. Concentration Cells

A concentration cell generates potential (E_{cell}) purely from the difference in concentration between two half-cells of the same materials. Since E°_{cell} is zero (as the half-reactions are identical under standard conditions), the Nernst equation simplifies to:

Concentration Cell Potential (Simplified Nernst):

$$E_{cell} = - (0.0592 V / n) \log Q$$

- The cell will run spontaneously until the concentrations in the two half-cells become equal ($Q=1$, $E_{cell}=0$).

5. Electrochemical Applications: Measurement of pH and K

Electrochemistry provides highly accurate methods for measuring chemical properties:

- Measurement of pH:** A glass electrode (pH electrode) develops a potential (E) that is proportional to the concentration of H^+ ions (or pH) in the solution.

Potential of a pH Electrode :

$$E = E^\circ + (0.0592 \text{ V}) \text{ pH}$$

- Equilibrium Constant (K):** At equilibrium, $E_{cell} = 0$, and $Q = K$. By setting the Nernst equation to zero, we can relate E°_{cell} to the equilibrium constant (K). This is the same relationship derived from thermodynamics ($\Delta G^\circ = -RT \ln K$).

Equilibrium Constant from E°_{cell} :

$$\log K = (n E^\circ_{cell}) / 0.0592 \text{ V}$$

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