Lecture 15 Thermodynamics of electrochemical systems

Goal of the lecture: To study the thermodynamic principles governing electrochemical systems, including electrode potentials, cell reactions, and the relationship between electrical energy and chemical energy.

Brief lecture notes: This lecture explores the thermodynamic foundations of electrochemical systems, focusing on the interrelation between chemical and electrical processes. Students will examine how the Gibbs free energy governs the spontaneity of electrochemical reactions and how equilibrium potentials are determined from standard thermodynamic data. The lecture also covers the Nernst equation, standard electrode potentials, and the effect of temperature and concentration on cell voltage. Applications include batteries, fuel cells, corrosion, and electrolysis, where thermodynamic analysis is crucial for understanding efficiency and reversibility

Main part

Electrochemical systems involve the conversion of chemical energy into electrical energy, or vice versa. A typical electrochemical system consists of two electrodes (anode and cathode) and an electrolyte that allows ionic conduction. From the thermodynamic point of view, an electrochemical reaction can be viewed as a redox process where oxidation and reduction occur at separate electrodes.

The electromotive force (EMF) or cell potential (E) represents the maximum potential difference between two electrodes under reversible conditions. It is directly linked to the Gibbs free energy change (ΔG) of the overall reaction:

$$\Delta G = -nFE$$

where

- n— number of moles of electrons transferred,
- F— Faraday constant (96485 C/mol),
- E— electromotive force (V).

A negative value of ΔGindicates that the reaction proceeds spontaneously in the direction of producing electrical energy.

Fundamental Thermodynamic Relationships

The first and second laws of thermodynamics govern energy transformation in electrochemical systems.
The change in Gibbs free energy can be expressed as:

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

where $\Delta H$is the enthalpy change and $\Delta S$is the entropy change. For an electrochemical cell operating reversibly, ΔGcorresponds to the maximum non-expansion work obtainable, i.e., electrical work.

At equilibrium, $\Delta G = 0$, and thus $E = 0$, meaning no net reaction occurs — the system is in electrochemical equilibrium.

Nernst Equation

The potential of an electrochemical cell under non-standard conditions can be calculated using the Nernst equation:

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

where

- E°— standard electrode potential,
- R— universal gas constant (8.314 J/mol·K),
- T— temperature (K),
- Q— reaction quotient.

This relation shows how the cell potential depends on temperature and reactant concentrations. It is crucial for predicting performance changes in real cells such as batteries and sensors.

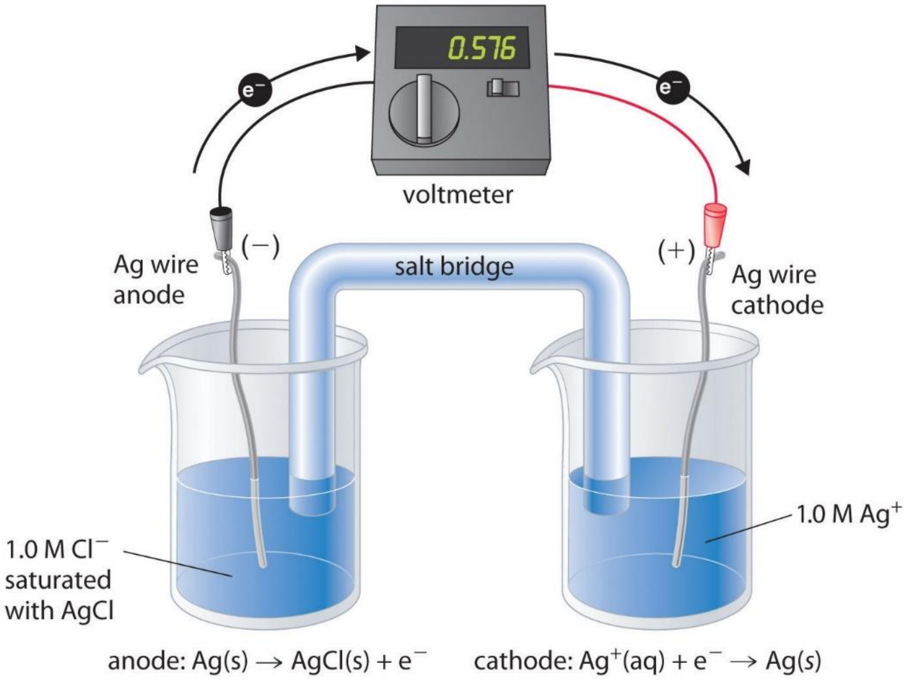

Figure 1. Schematic diagram of a galvanic (electrochemical) cell. The figure shows the anode and cathode compartments, salt bridge, and external circuit allowing electron flow. The direction of electron movement (from anode to cathode) and ion migration through the electrolyte are indicated, illustrating energy conversion between chemical and electrical forms.

Thermodynamic Quantities and Electrochemical Reactions

The three key thermodynamic quantities describing electrochemical systems are enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG). The relationships among them determine whether a reaction is spontaneous and how much electrical energy can be obtained.

For a reversible electrochemical process:

- If $\Delta G < 0$, the reaction is spontaneous (galvanic cell).
- If $\Delta G > 0$, the reaction requires electrical input (electrolytic cell).

Additionally, the temperature dependence of the EMF can be found by differentiating the Gibbs relation:

$$(\frac{\partial E}{\partial T})_P = \frac{\Delta S}{nF}$$

This allows determination of entropy changes from EMF–temperature data, linking measurable electrical parameters to fundamental thermodynamic properties.

Electrochemical Cell Representation and Operation

A galvanic cell is conventionally represented as:

$Zn \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu$

Here, the zinc electrode acts as the anode (oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$), and the copper electrode acts as the cathode (reduction: $Cu^{2+} + 2e^- \rightarrow Cu$). The salt bridge maintains electrical neutrality by allowing ion migration without mixing the solutions directly.

Table 1 : Thermodynamic Parameters of Selected Electrochemical Cells

Cell Reaction	n (mol e^-)	E° (V)	ΔG° (kJ/mol)	ΔH° (kJ/mol)
$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$	2	+1.10	–212.6	–218.0
$H_2 + ½O_2 \rightarrow H_2O$	2	+1.23	–237.1	–286.0
$Fe^{2+} + ½O_2 + H_2O \rightarrow Fe^{3+} + 2OH^-$	1	+0.77	–74.3	–92.0
$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$	2	+2.04	–394.0	–410.0

These values show that high standard EMF corresponds to large negative Gibbs free energy, confirming strong spontaneity.

Questions for Self-Control

1. How is Gibbs free energy related to the electromotive force of a cell?
2. What is the significance of the Nernst equation in determining cell potential?
3. How do temperature and concentration affect the voltage of an electrochemical cell?
4. What is the difference between galvanic and electrolytic cells from a thermodynamic point of view?
5. How can entropy change be determined from EMF–temperature dependence?

Literature

1. Çengel, Y. A., & Boles, M. A. Thermodynamics: An Engineering Approach. McGraw-Hill, 2020.
2. Atkins, P., & de Paula, J. Physical Chemistry. Oxford University Press, 2022.
3. Bard, A. J., & Faulkner, L. R. Electrochemical Methods: Fundamentals and Applications. Wiley, 2018.
4. Alberty, R. A. Thermodynamics of Biochemical Reactions. Wiley, 2003.
5. Newman, J., & Thomas-Alyea, K. E. Electrochemical Systems. Wiley, 2012.